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その他のタイトル          サファイア研磨における10nm以下のナノシリカ微粒子を適用した機能性ハイブリッドナノ微粒子の特异性に関する研究

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Novel characteristics of sub-10 nm silica particles for hybrid fine particles in chemical mechanical polishing of sapphire

サファイア研磨における10 nm以下のナノシリカ微粒子を適用した機能ハイブリッドナノ微粒子の特異性に関する研究

NATTHAPHON BUN-ATHUEK
Abstract

The ultrafine silica particles size of smaller than 10 nm exhibit the unique characteristics to produce the hybrid fine particles for improving the performance of chemical mechanical polishing (CMP) of sapphire. The hybrid fine particles are formed by ultrafine (4 nm) silica particles mixed with the larger (20 nm, 55 nm, and 105 nm) silica particles. The hybrid fine particles could control the chemical reactivity by ultrafine silica particles and the mechanical action from larger silica particles independently. The evanescent field light observation results specified that the ultrafine silica particles size of smaller than 10 nm are adsorbed on the surface of sapphire substrates. The transmission electron microscopy (TEM) and dynamic light scattering (DLS) results revealed the structure of hybrid fine particles. The hybrid fine particles were produced from ultrafine colloidal silica particles adhered to the surfaces of large silica particles thereby changed the surface condition by novel characteristics on the nano size particles.

The polishing results showed that the hybrid fine particles enabled a much higher performance of sapphire CMP than the conventional single-sized silica particles owing to the ultrafine silica enhanced the chemical reactivity to produce the reacted layer (alumina silicate). The material removal rate of sapphire was also increased due to the coefficient of friction (COF) of contact area between the sapphire substrate, polishing pad, and fine particles was increased. The hybrid fine particles might be modified by the ultrafine silica particles that adhered to the surface of larger silica particles.
Abstract

Chapter 2 shows the method to specify the dominant characteristics (mechanical action or chemical reactivity) of single-sized silica particles by using evanescent field light observation. We found that the boundary of dominant characteristics of ultrafine silica particles appear at the size of smaller than 10 nm.

Chapter 3 presents the method to prepare the hybrid fine particles by mixing process. The characterization of hybrid fine particles by TEM and DLS was also explained.

Chapter 4 describes the performance of sapphire CMP process by using the hybrid fine particles as the abrasive in the slurry. Furthermore, the method to investigate the effects of ultrafine silica particles on the material removal rate of sapphire was also presented.

Chapter 5 shows the optimization of hybrid fine particles. We found that the performance of sapphire CMP depends on the diameter size of large silica particle and the number ratio of ultrafine silica and larger silica particles in the slurry. The concept to optimize the performance of hybrid fine particles in sapphire CMP by varying the three parameters such as the diameter size of the larger silica particles, the reactivity, and the surface condition. The supposed model of sapphire removal by hybrid fine particles was also proposed.

Finally, we conclude that

1. The ultrafine silica particles size of smaller than 10 nm exhibited the unique characteristics, it performed high material removal rate.
2. The hybrid fine particles gave higher material removal rate for sapphire than single-sized silica slurries.
3. The ultrafine silica particles and hybrid fine particles also improved the surface roughness of sapphire.
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Chapter 1

Introduction

1.1 Overview of the thesis

This thesis presents the novel characteristics of fine silica particles to produce the hybrid fine particles for improving the performance of chemical mechanical polishing (CMP) of sapphire. The hybrid fine particles comprised by the ultrafine silica particles mixed with the larger silica particles. In this case, novel characteristics of fine silica particles exhibited the dominant factor (chemical or mechanical factors) of single-sized silica particles depends on the diameter size. Therefore, hybrid fine particle is the combination of high chemical reactivity by the ultrafine silica particles and high mechanical action from the larger silica particles. The polishing results confirmed that the hybrid fine particles produce the performance of sapphire CMP higher than the conventional single-sized silica particles. The optimization of hybrid fine particles was performed. The obtained results revealed the maximum point of polishing performance. The supposed model of material removal by hybrid fine particles was also proposed.

The thesis consists of six chapters covering the background, the importance of sapphire CMP process, the problem statement, the details of research methodology, results and discussion, and the conclusions. The overview of the research as shown in Figure 1.1.
Figure 1.1 Flow of research.
1.2 Necessary of chemical mechanical polishing

Recently, sapphire (single crystal of Al$_2$O$_3$) wafers have been widely used in a range of applications such as sensor, aerospace components, precision resistor, and optical because its excellent optical performance, superior mechanical properties, high melting point, good chemical stability, high corrosion resistance, low thermal expansion coefficient, extreme hardness and brittleness [1-3]. In addition, sapphire is an important material that is used as the substrate of light-emitting diodes (LEDs) owing to its ability to minimize defects in the GaN thin film on the substrate [1–5]. The applications of sapphire wafer as shown in Figure 1.2. Figure 1.3 shows the structure of the blue LED chip. To realize LEDs with low power consumption, a polished sapphire substrate with a very smooth planar surface without subsurface damage is required for the manufacture of high performance LEDs [11–18]. However, sapphire is a typical hard-to-process material against lapping and polishing because of those characteristics.

Zhu et al. [19] reported that; in several cases of the applications of sapphire substrate, the low surface damage and stringent surface quality (finish and flatness) are critical. These fine surface machining and polishing of ceramics (sapphire) may exceed 80% of total cost.
**Introduction**

Figure 1.2 Applications of sapphire wafer [6-10].
Figure 1.3 Schematic drawing of the structure of LED.
Introduction

Normally, the fabrication process to produce the very high quality of sapphire wafer as shown in Figure 1.4. First of all, the sapphire ingot is produced by EFG (Edge defined, Film-fed Growth) technique. After that, the slicing method is applied to cut the sapphire from the long cylinder become to thin chip (≈1 mm). The sapphire chip that was produced in this method appear a very high surface roughness. Therefore, to reduce the surface roughness and increase the planarization of sapphire chip. The grinding and lapping processes are conducted. In this case, the reduction of sapphire surface roughness is performed by the diamond particles in those processes about 3 hours. After the grinding and lapping process, the sapphire chip exhibit the very smooth and high planarized surface but still appear the subsurface damage, scratch, and defect owing to the hardness of diamond particles conducted during the grinding and lapping processes. Finally, the CMP process is applied to remove the subsurface damage, scratch, and defect from the sapphire wafer about 7 hours. The CMP process is a key technique to achieve the required surface quality of sapphire [21] due to the CMP process combines the chemical reactivity and the mechanical action to generate and remove the softer layer on the sapphire surface to produce a very smooth planar surface without subsurface damage, scratch, and defect.
Introduction

Figure 1.4 Flow chart of sapphire wafer fabrication [20].
Introduction

1.3 Chemical mechanical polishing of sapphire

Chemical mechanical polishing (CMP) is a process of wafer surface smoothing and planarization. The extreme smooth and flat surface of wafer without subsurface damage, deformations and scratches can be produced by using the CMP process. The CMP process combines chemical reactivity and mechanical action on the wafer surface. A simple configuration of CMP process as show in Figure 1.5

Normally, the wafer will be held by the polishing head. The wafer surface is attached to the backing film. The down-force pressure is applied to the polishing head to press the wafer surface on the polishing pad during the slurry is released to the polishing pad at the near center point of polishing pad. When the platen and polishing head are rotated, the slurry with the abrasive particles spread to the omnidirectional of polishing pad and are carried to the region between the wafer surface and the polishing pad. The slurry with the abrasive particles chemically react with the wafer surface. The reacted layer forms on the wafer surface. This reacted layer is softer than the abrasive particle and can be removed from the wafer surface by the both sliding and rolling abrasive particles [22].
Figure 1.5 Configuration of CMP process.
Introduction

However, the performance of polishing process can be simple expressed by Preston’s equation, which is the direct proportion to the pressure of wafer and the velocity of polishing pad as shown in Equation 1.1 [23].

\[ \text{Rate} = K_p \cdot P \cdot \frac{\partial s}{\partial t} \]  

(1.1)

where \( K_p \) is the Preston coefficient, \( P \) is the down-force pressure, and \( \frac{\partial s}{\partial t} \) is the linear velocity of the polishing pad. However, the exact mathematic model of CMP process is still not conclude yet.

Recently, CMP process has been widely used for achieving a global planarization and very smooth surface in semiconductor devices manufacturing such as integrated circuit (IC), light emitting diodes (LEDs), etc. The CMP market size rapidly increased from about $300-400 millions in 1997 to $3.32 billion in 2014 [24-25]. The CMP process requires the several consumables. The slurry cost is a major component (up to 50%) of the overall cost in CMP consumables as reported by Bahr et al. [26]. Furthermore, we can see that the CMP consumable of the slurry market is growing at a higher value than the polishing pad and the trend is constantly increasing as shown in Figure 1.6.

This information exhibited that the reason why, recently, so many researchers focused on the development of the abrasive particles in the slurry such as using composite particles as abrasive in the slurry and the improvement of polishing performance such as developing the soft polyurethane material for polishing pad [28-31].
Introduction

Figure 1.6 Growth of CMP slurry and pad markets [27].
Introduction

A brief of the properties of sapphire as the substrate has been explained in Sect 1.2. The performance of devices that made by sapphire wafer depends on the quality of sapphire surface [21][32]. Therefore, sapphire wafers have to realize an extremely smooth planar surface without subsurface damage to manufacture a high performance of devices with low consumption. Although, sapphire is a typical hard to-process material against lapping and polishing because it exhibits extreme hardness and brittleness [33-34]. Figure 1.7 shows the hardness of sapphire compared with another elements in hardness Mohs scale. However, the sapphire wafer could be polished using the silica particles as abrasive into the slurry in CMP process. Although the silica particles have a lower hardness than the sapphire wafer but the chemical reactivity produced on the between silica particles and the sapphire surface, is softer than the silica particles [37]. According to Wang et al. [38] reported that the use of colloidal silica particles as abrasive in the slurry for sapphire polishing is widely researched and developed by many researchers due to the advantage of disperity and stability of silica particles. In addition, the colloidal silica particles could produce a believable material removal rate of sapphire owing to the chemical reactivity between silica particles and sapphire wafer.
Figure 1.7 The Mohs scale of hardness [35-36].
The brief of the mechanism of sapphire CMP using the silica particles as abrasive in the slurry as shown in Figure 1.8. We can explain as following:

1.) The silica particles that dispersed into the slurry are delivered to the contact area (wafer surface) by the polishing pad.

2.) The silica particles in the slurry, chemically react with the sapphire surface.

3.) The chemical reaction produce the reacted layer. This reacted alumina layer is softer than the silica particles.

4.) The silica particles remove the reacted layer from the sapphire surface by abrasion.
Figure 1.8 The mechanism of sapphire CMP using silica particles as abrasive
(a) silica particles are delivered to the sapphire surface by polishing pad, (b) silica particles contact to the wafer surface, (c) silica particles produce the reacted layer
(d) silica particles remove the reacted layer from the surface.
1.4 Advantage and disadvantage of sapphire CMP

The traditional sapphire CMP using the silica particles as abrasive in the slurry has been widely applied as the important key to produce a global and local planarization surface of sapphire wafer. The advantages of traditional sapphire CMP process; there are a high credibility to provide the ultra-smooth surface roughness and very high planarized of sapphire wafer [39-40]. In contrast, the disadvantages of traditional sapphire CMP process are, it need to take a long time and increase a consumable cost in polishing process. In addition, the material removal rate obtained using traditional silica particles is low [21][39-40].

1.5 Issue of sapphire CMP

The sapphire CMP process exhibits the advantages to remove the subsurface damage that occurred during the grinding and lapping process to produce the very smooth and planarized surface of sapphire wafer as explained in Sect 1.2. Normally, the CMP process need to spend for a long time (about 7 hours). In addition, the mechanism and phenomenon of material removal during polishing process are still difficult to specify because limitation of the observation devices and the structure of CMP machine.

Although, the development of the sapphire CMP process has been experimentally performed at several institutions and companies focused on slurries such as colloidal silica slurry and polishing pads [41-42]. However, the material removal rate (MRR) of sapphire using silica particles as abrasive in CMP is still very low and high costs due to the stable chemical properties of sapphire and high costs result from the need for very long polishing times [43]. Thus, the CMP process with a high material removal rate of sapphire to maintain a very smooth
planarized surface must be developed to manufacture substrates. In addition, the demand in the increasing of the performance of sapphire CMP is still challenge in the present.

1.6 How to increase the performance of sapphire CMP

The method to increase the performance of CMP process by improving the CMP device have been reported by another researchers. Several techniques are shown as following:

(1) Sakamoto et al. [44] proposed the Ultraviolet-assisted polishing of hard to process substrate as shown in Figure 1.9. This method promoted the performance of polishing process by using a photochemical reaction for mechanical removal induced by ultraviolet ray irradiation.

(2) Doi et al. [45] proposed the innovative plasma fusion CMP to establish a high-efficiency/high-quality polishing process of the hard-to-process materials as shown in Figure 1.10. This method showed the superior performance of polishing process.

Unfortunately, these processes are required the special devices and complicated technique to install on the CMP machine. However, our laboratory’s research have focused on another way to increase the performance of CMP process by studying the cause and effect of material removal rate. Normally, the three main parameters that affect to the performance of polishing process could be written as following [46-47].

1.) The slurry: concentration, pH, size, stability of the suspension, etc.

2.) The polishing pad: pad velocity, conditioning, pad hardness, etc.

3.) The wafer: wafer velocity, pressure, wafer size, etc.

The summarized parameters in polishing process as shown in Figure 1.11. We can see that abrasive particle (slurry) is one of parameters that affect to the polishing process.
Introduction

Figure 1.9 The UV-assisted polishing in CMP device [44].

Figure 1.10 The plasma fusion CMP system [45].
Figure 1.11 Three major categories of the input variables.
In addition, the abrasive particles exhibit both chemical and mechanical factors during polishing process. Therefore, we expect that the performance of polishing process can be improved by focusing on the abrasive particles. In this case, hybrid particles is one kind of abrasive that produce the higher performance than the conventional abrasive. Many researchers used the hybrid particles as abrasive in the slurry. The hybrid particles used in CMP process are listed as following:

(1.) K. Sakai [48] reported that the hybrid particles comprised by ceria particles mixed with diamond particles (as shown in Figure 1.12) improved the material removal rate and surface roughness of sapphire wafer.

(2.) Mudhivarthi et al. [49] reported that hybrid abrasives are developed where the composition of the polymeric particles formed via colloidal precipitation (as shown in Figure 1.13) is modified with inorganic segments to reduce surface damage during CMP. The polishing results confirmed that the surface roughness of wafer was improved.

Although, the characteristics and removal mechanism of those hybrid particles are not clearly expressed and cannot specify the dominant factor of fine particles in polishing process but the performance of CMP process could be improved very well. Therefore, our concept to solve the issue of CMP process is fabricate the hybrid fine particles by using the combination of different advantage factors from two kinds of particles. In this case, we define the assumption of hybrid fine particles as explained in next section.
Introduction

Figure 1.12 The hybrid particles comprised by ceria and diamond particles [48].

Figure 1.13 Hybrid particles developed by polymeric particles and inorganic segments [49]
1.7 Our assumption to increase the performance of sapphire CMP

Our challenge is how to increase the performance of sapphire CMP? We found that the performance of polishing process was improved by using the hybrid particles. In addition, the mechanical and chemical factors are the importance parameter in CMP process. Therefore, the assumption to produce hybrid fine particles as following:

1) The hybrid fine particles will be formed by the ultrafine and larger silica particles to combine the both dominant factors in polishing process owing to the ultrafine and larger silica particles might mainly perform the different dominant factor as the chemical and mechanical factors depend on the characteristics of fine silica particles.

2) The proposed hybrid fine particles can increase the performance of sapphire CMP process by controlling the chemical and mechanical factors of ultrafine and larger silica particles.

The concept of hybrid fine particles as shown in Figure 1.14
**Hybrid fine particles**

*High chemical reactivity?? or High mechanical action??*

*High mechanical action?? or High chemical reactivity??*

The ultrafine silica particles + The larger silica particle

*The both dominant will be combined*

*Increase the performance of CMP*

*Sapphire CMP*

Figure 1.14 Assumption to produce the hybrid fine particles.
1.8 Research purpose

The specific objectives of this thesis can be written as following:

1) To specify the characteristics of fine silica particles.
2) To fabricate the hybrid fine particles by the ultrafine and larger silica particles.
3) To improve the performance of sapphire CMP (material removal rate and surface roughness) by using the hybrid fine particles
4) To propose the mechanism of material removal by hybrid fine particles in sapphire CMP.
Chapter 2

Characteristics of fine silica particles in sapphire CMP

2.1 Introduction

The characteristics and material removal mechanism of fine silica particles in polishing process is the importance point to improve the polishing performance owing to the abrasive particles is one of major parameters that exhibit both chemical and mechanical factors. However, the dominant factor of fine silica particles in sapphire CMP is still unspecified. Therefore, we have to study and specify the characteristics and material removal mechanism of fine silica particles for improving the performance of sapphire CMP.

The sapphire CMP process has been experimentally performed on the fine silica slurry, although the material removal mechanism is still unclarified [21][33][50-54]. For the material removal mechanism, Choi et al. [22] predicted that the behavior of colloidal silica fine particles could be due to their two types of movement, namely, sliding and rolling, in the slurry layer between the surface of polished substrate and polishing pad as shown in Figure 2.1. Luo et al. [55] reported that the slurry react with the wafer surface and produced the passive layer before the abrasive particles were carried by polishing pad to remove the reacted layer from the wafer surface as shown in Figure 2.2. Kimura et al. [56] reported that the bonding between fine particles and reacted layer is larger than the bonding between the reacted layer and wafer surface before the fine particles remove the reacted layer as shown in Figure 2.3.
Figure 2.1 The behavior of fine particles (a) sliding and (b) rolling modes.
Figure 2.2 The material removal mechanism proposed by Luo et al [55].

Figure 2.3 The material removal mechanism proposed by Kimura et al [56].
In addition, other researchers studied the behavior of abrasive particles in polishing process. They reported that the material removed from polished substrates adhered to fine particles after the CMP, which is increase in abrasive particle size in the slurry [57-61]. However, the characteristics of abrasive particles during CMP are still unclarified and must be studied further.

2.2 The mechanism of sapphire removal by silica particles in sapphire CMP.

In this research, for the understanding on the characteristics of silica particles as abrasive during polishing, we studied the change in fine particle size in slurries including its effect on the performance of the CMP process. In this case, the fine silica particle might be damaged by the use of a substrate harder than silica particles during CMP. Therefore, we predict that the material removal rate will decrease with increasing of polishing time owing to the degradation of particles in the slurry.

Furthermore, the mechanism of sapphire removal by the silica particles will be discussed. After that, we expect that the understanding of sapphire CMP process using the single-sized silica particles as abrasive will be applied to specify the characteristics of fine silica particles in sapphire CMP process.
2.2.1 Experiments method

Polishing experiments

The polishing experiments were conducted by using a CMP machine (IMT Rana-30) as shown in Figure 2.4 and fine silica particles as abrasives. The conditions for these experiments are shown in Table 2.1. All experiments were performed by using a reuse slurry system without a filter as shown in Figure 2.5. The material removal amount and the material removal rate of sapphire were calculated by considering the wafer loss weights before and after CMP. The weight of sapphire wafers was measured using an electronic balance (A&D BM-20).

Table 2.1 Polishing conditions.

<table>
<thead>
<tr>
<th>Slurry</th>
<th>fine silica, pH 11 adjusted using KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>20 nm (NALCO 1040) and 55 nm (NALCO TX15582)</td>
</tr>
<tr>
<td>Concentration</td>
<td>10 wt%</td>
</tr>
<tr>
<td>Wafer</td>
<td>Sapphire (C-plane)</td>
</tr>
<tr>
<td>Polishing pad</td>
<td>Suba600</td>
</tr>
<tr>
<td>Polishing time</td>
<td>0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h</td>
</tr>
<tr>
<td>Pad conditioning</td>
<td>Nylon brushing 5 min before each case</td>
</tr>
<tr>
<td>Platen/Carrier speed</td>
<td>47 / 73 rpm</td>
</tr>
<tr>
<td>Polishing pressure</td>
<td>0.138 MPa</td>
</tr>
<tr>
<td>Slurry weight</td>
<td>320 g</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>60 ml/min</td>
</tr>
</tbody>
</table>
Characteristics of fine silica particles in sapphire CMP

Figure 2.4 Photograph of CMP machine IMT Rana-30.

Figure 2.5 Schematic of CMP device with reuse slurry system.


Characteristics of fine silica particles in sapphire CMP

Fine silica particle characterization

Silica particles size were measured before and after CMP by dynamic light scattering (DLS; Malvern ZETASIZER Nano S) as shown in Figure 2.6. Their shape, and surface characteristics were observed by transmission electron microscopy (TEM; FEI Tecnai G2 Spirit) as shown in Figure 2.7.

Analytical of silica particle composition

Silica particles in slurries after 3 h of CMP were filtered by a vacuum filtration method. After liquid and solid (silica particles) phases were separated, the silica particles were dispersed in deionized (DI) water. Then, liquid and solid (silica particles) phase samples in DI water were analyzed by X-ray fluorescence spectrometry (XRF; Shimadzu EDX-7000).
Figure 2.6 Photograph of dynamic light scattering (Malvern ZETASIZER Nano S).
Figure 2.7 Photograph of transmission electron microscopy (TEM; FEI Tecnai G2 Spirit).
2.2.2 Experimental results

Fine particle characterization

Figure 2.8 shows the increase in silica particle size measured by DLS after 3 h of CMP. The particle size after CMP was larger than that before CMP. Figures 2.9(a) and 2.10(a) show the TEM images of silica particles with sizes of 20 and 55 nm obtained before CMP, respectively. We observed that the particles were almost round, uniform, well distributed, and monodispersed. However, the size and shape of some silica particles before CMP became larger and more nonuniform than those after CMP as shown in Figures. 2.9(b) and 2.10(b). In addition, the surface reactivity of fine particles changed.

Analysis of fine particles in slurry after polishing

To specify the element coated on the silica particle surface, Table 2.2 shows XRF analysis results that reveal the alumina intensity in the liquid (filtrate) and solid (silica particles) phases of the filtered silica slurry size of 55 nm. These results confirm that aluminum, which was removed from the sapphire substrate, was divided into two parts. The first part, which is the alumina element smaller than a pore on a membrane filter, can infiltrate the liquid phase. The other part, which is the alumina element that aggregates on the silica particle surface, cannot infiltrate the liquid phase, increasing the size of abrasive particles as shown in Figure 2.11.
Figure 2.8 Increase in silica particle size after CMP for 3 h.
Figure 2.9 TEM images of silica particles with size of 20 nm (a) before and (b) after CMP.

Figure 2.10 TEM images of silica particles with size of 55 nm (a) before and (b) after CMP.
Characteristics of fine silica particles in sapphire CMP

On the other hand, at the silica slurry size of 20 nm, we observed the alumina intensity in the silica particle phase only. In this case, a few alumina elements were removed from the sapphire substrate (see Sects. Material removal amount (MRA) of sapphire and Material removal rate (MRR) of sapphire in pages 40 and 42 respectively) and almost all those alumina elements aggregated on the silica particles. From this phenomenon and the DLS spectral results, we observed that the increase in particle size in slurries was proportional to the polishing time as shown in Figure 2.12. In addition, the particle size in slurries markedly changed with the action of particles on the sapphire substrate during the actual CMP operation, which was not observed without the polishing process.

Table 2.2  XRF analysis results of the filtered slurry after CMP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Liquid phase (wt%)</th>
<th>Silica particle phase (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>Si</td>
</tr>
<tr>
<td>20 nm silica slurry</td>
<td>99.492</td>
<td>0.455</td>
</tr>
<tr>
<td>55 nm silica slurry</td>
<td>99.939</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Figure 2.11 Alumina element and silica particles after filtration.
Figure 2.12 Increase in silica particle size in slurries
(a) 20 and (b) 55 nm with dependence on CMP time.
**Characteristics of fine silica particles in sapphire CMP**

**Material removal amount (MRA) of sapphire**

In this study, we can see an almost linear correlation between the increase in particle size as a function of volume and MRA as shown in Figure 2.13. The increase in particle volume at the silica slurry size of 55 nm was larger than that at the silica slurry size of 20 nm, and the MRA of sapphire CMP at the slurry size of 55 nm was much larger than that at the slurry size of 20 nm. Zhou et al. [62] reported that small fine particles exhibit a much smaller mechanical effect than large fine particles, but a higher chemical activity because small fine particles need a smaller activation energy to react with the sapphire substrate surface than do large fine particles.

Our experimental results suggest that the level of aggregation of silica particles of 55 nm diameter with the removal of the material from the substrate is higher than that of silica particles of 20 nm diameter, although small fine particles are larger in number and surface area to react with the substrate surface at the same slurry concentration. Therefore, the increase in fine particle size might be caused by a mechanical factor, because the mechanical action for the silica particle size of 55 nm is higher than that of the silica particle size of 20 nm.
Figure 2.13 Increase in silica particle size as a function of volume and MRA of sapphire.
Material removal rate (MRR) of sapphire

Figure 2.14 shows that the MRR of sapphire obtained using silica particles with a size of 20 nm produced is lower than that obtained using silica particles with a size of 55 nm because the mechanical action for the silica particle size of 20 nm is lower. These results indicate that large particles have a higher indentation ability (mechanical effect) than small particles as reported by Lei et al. [63]. In addition, we observed that the difference between the particles sizes of 20 and 55 nm, the MRR for the silica particle size of 20 nm gradually decreases from 0.42 to 0.21 μm/h from the polishing time of 0.5 to 3.0 h, respectively, which is caused by the gradual decrease in reactivity surface area at the particle size of 20 nm with the aggregation of alumina elements that increase the fine particle size. In contrast, the MRR for the silica particle size of 55 nm increases from 1.42 to 2.41 μm/h from the polishing time of 0.5 to 2.5 h, respectively. These results suggest that the increases the MRR for the silica particle size of 55 nm, owing to the decrease in reactivity surface area at the particle size of 55 nm is slower than particle size of 20 nm because chemical reaction rate of large particles is lower than small particles as reported by Zhou et al. [62]. After that, the MRR for the silica particle size of 55 nm gradually decreases to 2.10 μm/h at the polishing time of 3 h. However, when we considered the polishing time of 4 h, the silica particle sizes of 20 and 55 nm produce MRR values of 0.07 and 1.57 μm/h respectively. This confirms that the decreases in MRR depends on the decrease in surface area reactivity caused by Al coated on fine particles.
Characteristics of fine silica particles in sapphire CMP

Figure 2.14 MRR of sapphire obtained using silica particles with a sizes of (a) 20 and (b) 55 nm with dependence on CMP time.
The supposed mechanism of sapphire removal by silica particles

Figure 2.15 shows the supposed mechanism of sapphire removal by fine silica particles based on the obtained results as explained. When the fine silica particles chemically react with the sapphire surface, an alumina layer forms on the sapphire substrate [64].

The chemical reaction on that layer was divided into two steps: sapphire reacts with $\text{H}_2\text{O}$ to produce sapphire hydrate as shown by [13][65]

\[
\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3,
\]

\[
\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3.
\]

Then, the silica particles become in contact with sapphire/sapphire hydrate and generate alumina silicate as shown by [65-66]

\[
2\text{SiO}_2 + 2\text{Al(OH)}_3 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O},
\]

\[
2\text{SiO}_2 + \text{Al(OH)}_3 + \text{Al(OH)}_3 \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O},
\]

\[
2\text{SiO}_2 + \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}.
\]

This reacted alumina layer (alumina silicate) is softer than the silica particle [66-69] and can be removed from the sapphire surface. After that, during both sliding and rolling [22], silica particles and some alumina molecules aggregate and increase the particle size. The remaining alumina element that does not aggregate with silica particles will be dispersed in the slurry.
Figure 2.15 Supposed mechanism of sapphire removal by fine silica particles.
Summary of mechanism of sapphire removal by silica particles

In this chapter, the characteristics of fine silica particles in sapphire CMP were studied. We found as following:

Fine silica particles with different sizes were used in sapphire polishing. We observed the increase in silica fine particle size by TEM and DLS. The obtained results suggest that sapphire is removed by adhering such a material to fine silica particles during CMP. XRF revealed that the alumina element (alumina silicate) from sapphire wafer coated to fine silica particles, decreasing their surface area reactivity. Therefore, MRR decreased with increasing of polishing time owing to the degradation of particles in the slurry. Finally, the increase in silica particle size was observed to be proportional to the MRA of sapphire and the main factor of such an increase is the down force per particle (mechanical effect).

Hence, we found the surface variation of fine silica particles as abrasives in the slurry for the CMP of sapphire. In addition, we observed that the particles size is one of factor that affects to the surface variation of silica particles. In order to more understand about the fine silica particles, therefore, the characteristics of fine silica particles will be studied and explained in Sect. 2.3.
2.3 Characteristics of fine silica particles on the polishing ability

Based on the polishing results as explained in Sect. 2.2, we found that the tendency of material removal rate of sapphire obtained using the single-sized silica particles increased with increasing of the particle size as shown in Figure 2.16. In this case, we assume that the polishing ability of fine silica particles might depends on the effects of chemical and mechanical factors of fine silica particles in sapphire CMP. In order to study the characteristics of fine silica particles and specify the dominant factor from chemical and mechanical factors, the smaller and larger silica particles than 20 nm and 55 nm respectively, will be used as abrasive in sapphire CMP.

2.3.1 Experiments method

Slurry preparation

The 4 nm silica slurry (NALCO 1115) as the ultrafine colloidal silica particles, 20 nm (NALCO 1040), 55 nm (NALCO TX15582), and 105 nm (NALCO 2329 Plus) silica slurries as the large silica particles, were used as the abrasive particles in the single-sized silica slurries. The slurries were adjusted to a pH of 11 by the addition of either KOH or H$_2$SO$_4$, as appropriate. Details of the prepared slurries are shown in Table 2.3.

<table>
<thead>
<tr>
<th>(1) Diameters of fine particle</th>
<th>4, 20, 55, and 105 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) Concentration</td>
<td>5 wt%</td>
</tr>
<tr>
<td>(3) pH</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 2.16 Tendency of MRRs obtained using the single-sized of silica particles based on the conventional model.
Polishing experiments

The polishing experiments were conducted by using a CMP machine (IMT Rana-30) as explained in Sect. 2.2.1. The conditions for these experiments are shown in Table 2.4. The material removal rates of sapphire were calculated by considering the wafer loss weights before and after CMP. The weight of sapphire wafers was measured using an electronic balance (A&D BM-20). The surface roughnesses of the sapphire substrates were measured by atomic force microscopy (AFM; SII SPA300HV) before and after polishing.

Table 2.4 Polishing conditions.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>mm</th>
<th>Polishing pad</th>
<th>Suba600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polishing time</td>
<td>min</td>
<td>Conditioning time</td>
<td>5</td>
</tr>
<tr>
<td>Polishing pad seasoning</td>
<td></td>
<td>Polishing pressure</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Platen/Carrier</td>
<td>60/60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Slurry flow rate</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Number of samples</td>
<td>3</td>
</tr>
<tr>
<td>Sapphire (Al₂O₃) φ 25.4, t = 1</td>
<td></td>
<td>Nylon brushing</td>
<td></td>
</tr>
</tbody>
</table>
Polishing experiments

Figure 2.17 shows that the MRR of sapphire after 3 h of CMP using single-sized silica slurries increased with increasing particle size from 20 to 55 to 105 nm. The 105 nm slurry gave the highest MRR, close to that achieved by the ultrafine silica alone. In addition, the surface roughnesses of sapphire wafer obtained using silica particles increased with increasing of particles size from 4 nm to 105 nm respectively. These results indicated that the large silica particles with size of 105 nm produced the high material removal rate by the high mechanical action. On the other hand, the ultrafine silica particles also produced the high material removal rate by the low mechanical action. In this case, we expect that the chemical reactivity might be the reason.

2.3.2 Study on chemical reactivity of single-sized silica particles

As we mentioned that the colloidal silica particles has been widely used as abrasive in sapphire CMP due to a silica particles could provide an acceptable removal rate, because the silica particles chemically react with the sapphire surface [42][64][66]. This reacted layer (alumina silicate) is softer than the silica particle and can be removed from the sapphire substrate [66-69]. Normally, the material removal rates (MRRs) of sapphire obtained using a silica slurry increased with the increasing of the abrasive size owing to the increase in indentation ability of fine particles under the same pressure [42]. However, our previous results in Sect. 2.3.1 showed the different characteristics of ultrafine silica particles and the large silica particle with size of 105 nm. We predict that the dominant factor in ultrafine silica particles and the large silica particles might be different.
Characteristics of fine silica particles in sapphire CMP

Figure 2.17 Polishing results of sapphire CMP obtained using single-sized silica particles.
Our assumption to specify the characteristics and the dominant factor of fine silica particles are the amount of alumina silicate increases with increasing of the number of silica particles that attached on the sapphire surface as much as possible as shown by the following equation

1.) Sapphire reacts with H₂O to produce sapphire hydrate

\[ Al_2O_3 + H_2O \rightarrow 2AlO(OH), \]

2.) Silica particles contact to the sapphire hydrate and produce the alumina silicate

\[ 2SiO_2 + 2AlO(OH) + H_2O \rightarrow Al_2Si_2O_7 \cdot 2H_2O \]

Figure 2.18 shows the assumption of reacted layer (alumina silicate). The occurring of reacted layer depends on the distance between fine silica particle and sapphire surface. The silica particle approach to the sapphire surface should produce a higher alumina silicate than the silica particles that be far away from the sapphire surface. Therefore, based on these assumption, the mechanism of high material removal in sapphire CMP with the ultrafine silica particles size of 4 nm compared with the larger silica particles with sizes of 20, 55, and 105 nm, was investigated by using the zeta potential to reveal the phenomenon of material removal by the silica particles from the sapphire surface because we expected that the number of ultrafine silica particles might approach to the sapphire surface by the electrostatic force between the silica particles and sapphire substrate much higher than the large silica particles.
Characteristics of fine silica particles in sapphire CMP

Figure 2.18 Assumption of silica particles approach to sapphire substrate by electrostatic force and produced the reacted layer.
**Zeta potential measurement**

The zeta potential of ultrafine silica particles and larger silica particles were measured by using zeta potential measuring function in dynamic light scattering (DLS; Malvern ZETASIZER Nano ZS). The samples were kept in the folded capillary cell (DTS1070) before inserted to the sample holder in the machine.

**Zeta potential results**

Figure 2.19 exhibits the zeta potential obtained using single-sized silica slurries decreased with increasing of particle size from 20 to 55 to 105 nm. The ultrafine silica particles (4 nm) produced the lowest zeta potential. In this case, we found that the particles with a same element (silica) and condition of pH value possessed a different zeta potentials.

However, the zeta potential of sapphire wafer is about -12.5 mV [13]. This is the same charge with the single-sized silica particles. These results indicated that the force between sapphire substrate and fine silica particles is should be the repulsive force. This mean the single-sized silica particles cannot contact to the sapphire surface as shown in Figure 2.20 but these results are conflict with our polishing results. Hence, we concluded that the zeta potential cannot explains the phenomenon of high removal rate produced by the ultrafine silica particles and the larger silica particles. Therefore, we need to use another method to investigate the material removal mechanism and specify the characteristics of ultrafine silica particles and large silica particles. That method has to observe the phenomenon of sapphire surface and fine silica particles. Panart et al. [70-72] proposed the method to observe the fine particles that adhered to an interface area by applying an evanescent field. Therefore, we consider to use the evanescent field to observe the phenomenon of fine silica particles and sapphire substrate.
Characteristics of fine silica particles in sapphire CMP

Figure 2.19 Zeta potential obtained using single-sized silica slurries.
Figure 2.20 Schematic of electrostatic force of fine silica particles and sapphire surface based on zeta potential results.
The evanescent field

Figure 2.21 shows the characteristics of evanescent field is produced by the incident light (green light laser) to the interface area between the two kinds of material with a different refractive index (n1, n2). When the angle of incident light is larger than the critical angle, the total reflection of light will occur. The evanescent field appears on the opposite side of the reflecting light. The scattering light will be arisen when the fine particle comes into the evanescent field. Normally, the intensity of scattering light varies by the distance (the depth) of the fine particle and the interface area [72-73]. Therefore, based on the properties of the evanescent field, the intensity of scattering light can be detected and indicates the characteristics of fine particles.

The samples preparation to investigate the mechanism of high material removal

The silica slurries with particle sizes of 4 nm (NALCO 1115), 20 nm (NALCO 1040), 55 nm (NALCO TX15582), and 105 nm (NALCO 2329 Plus) were prepared by adding a DI-water to dilute a concentration. After mixing, the slurries were adjusted to a pH of 11 by the addition of KOH. In this experiment, a mixed DI-water and KOH at a pH of 11 was also prepared as a sample.
Figure 2.21 Schematic expression of observation of scattered light using the evanescent field.
Detecting the intensity of scattering light

The intensity of scattering light was detected by the optical system as shown in Figure 2.22. The samples were placed, on the center of the sapphire wafer. After adjusting the focus of objective camera to detect the intensity of scattering light, the green light is irradiated from the laser source to the interface area of the slurry layer and sapphire substrate. We then tracked the time from which the silica slurry was released from the dropper until 60 seconds. The change in the intensity of scattering light produced by the silica particles in the slurry was calculated by integrating the area under graph of the intensity scattering light using

\[ \Delta I = \int_{t_1}^{t_2} I_0(t) dt \]  

(2.1)

where \( \Delta I \) is the change in the intensity of scattering light, \( I_0(t) \) is the intensity of scattering light with dependence on a time, \( t_1 \) is starting time, and \( t_2 \) is stopping time.

The results of scattering light in the evanescent field

The results of intensity of scattering light obtained using the samples of single-sized silica slurries, and DI-water with the pH of 11 are shown in Figure 2.23. The ultrafine silica particles gave the highest intensity of scattering light. In contrast, the slurries with particle sizes of 20, 55, and 105 nm produced a lower intensity (approximately 0.2 times) of scattering light than the ultrafine silica particles. Furthermore, the intensity of scattering light produced by the DI-water (added KOH) is much smaller than those silica slurries owing to the absence of fine particles. These results confirm that the scattering light was occurred by a fine silica particles moving into the evanescent field in the slurry layer.
Figure 2.22 Schematic of optical system for detecting the intensity of light scattering.
Figure 2.23 Intensity of scattering light after dropped the samples on sapphire wafer.
Discussion of the results of scattering light intensity

The results indicated that the ultrafine silica particles come to a nearer interface, and enhance a higher chemical reactivity with alumina element on the sapphire substrate to produce the reacted alumina layer than those larger silica particles with sizes of 20, 55 and 105 nm. Based on the results of scattering light including the performance of sapphire polishing (removal rate and surface roughness) as reported in Sect 2.3.1. The existence of ultrafine silica particles might be a boundary of the dominant factors of chemical reactivity and mechanical action of fine silica particles as shown in Figure 2.24. We found that the surface roughness of sapphire CMP obtained using a silica slurry with a particles sizes of larger than 10 nm is almost proportional to the polishing rate as a function of silica particle size in the slurry.

These results confirmed that the silica particles with sizes of larger than 10 nm possess the mechanical action as the dominant factor for sapphire polishing process due to the increase in the silica particle size, which produce both the higher MRR but lower quality of surface roughness of sapphire wafer. In contrast, the ultrafine silica particles achieved both the high MRR and very smooth surface roughness of sapphire, although the diameter size is much smaller. These results indicated that the chemical reactivity formed by using the ultrafine silica particles is a dominant factor for sapphire polishing, and might have a higher rate, according to the results of scattering light. Therefore, we predict that the boundary of fine particle size to indicate a dominant factor between mechanical and chemical factors is about 10 nm.
Figure 2.24 Boundary of chemical and mechanical factors in sapphire CMP
2.3.3 The summary of novel characteristics of fine silica particles

The detecting results showed that the intensity of scattering light produced by ultrafine silica particles is much higher than those of larger silica particles sizes of 20, 55, and 105 nm. We conclude as following.

(1) Evanescent field could detect the absorption of fine silica particles on the sapphire surface

(2) The intensity of scattering light indicated the ability of material removal by fine silica particles.

(3) The ultrafine silica particles exhibited the unique characteristics, it might promotes a chemical reactivity to be evidently a main factor of silica particle with size smaller than 10 nm on the sapphire surface.
Chapter 3

The hybrid fine particles

3.1 Hybrid particles

To increase the performance of sapphire CMP, the polishing process must be improved to produce a very high material removal rate with ultra-smooth surface roughness. Many researchers improved the performance of sapphire CMP using hybrid particles in the slurry. Lei et al. reported that the use of Cu, Zn, La, and Ce as chemical modifiers of colloidal silica abrasives produced a higher MRR and lower surface roughness of sapphire than that of a pure silica abrasive [74-77]. A similar performance improvement was achieved using Ag and Mn to dope colloidal silica abrasives, as reported by Zhang et al. [78-79]. However, the hybrid particles as mentioned above are still difficult and complicated in preparation. Other researchers have studied the use of different sizes of colloidal silica abrasives in the polishing slurry. Lee et al. reported that a mixture of two different sizes and shapes of silica abrasives for oxide CMP could produce high removal rates when used at an appropriate mixing ratio [80-81]. However, the above hybrid particles need the special technique to produce.

In our research, we found the novel characteristics of ultrafine silica particles and larger silica particles, which appear the chemical and mechanical factors as the dominant factor respectively. Therefore, the hybrid fine particles are prepared by using the very simple method to combine the both dominant factors of fine particles and use as the abrasive in sapphire CMP.
3.2 Preparation of hybrid fine particles

The hybrid fine particles comprised 4 nm silica slurry (NALCO 1115) as the ultrafine silica particles mixed with 20 nm (NALCO 1040), 55 nm (NALCO TX15582), or 105 nm (NALCO 2329 Plus) silica slurries as the large silica particles. Details of the prepared slurries are shown in Table 3.1. The slurries were adjusted a pH by the addition of either KOH or H$_2$SO$_4$, as appropriate. The sizes of the fine silica abrasives were measured before and after mixing by dynamic light scattering (DLS; Malvern ZETASIZER Nano S). Their shape and surface characteristics were observed by transmission electron microscopy (TEM; FEI Tecnai G2 Spirit; accelerating voltage: 120 kV). The silica samples for TEM observation were prepared by dropping the samples on the grids (QUANTIFOIL® R 2/2) and quickly embedded into the ethane that cooling by the liquid nitrogen by using a plunger (LEICA EM-GP) to produce the amorphous ice after instant freezing as shown in Figure 3.1.

Table 3.1 Properties of (a) single-sized silica particles and (b) hybrid fine particles.

<table>
<thead>
<tr>
<th>(a)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Diameters of fine particle</td>
<td>4, 20, 55, and 105 nm</td>
</tr>
<tr>
<td>(2) Concentration</td>
<td>5 wt%</td>
</tr>
<tr>
<td>(3) pH</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Diameters of fine particle</td>
<td></td>
</tr>
<tr>
<td>(1.1) Ultrafine silica particle</td>
<td>4 nm</td>
</tr>
<tr>
<td>(1.2) Large silica particle</td>
<td>20, 55, and 105 nm</td>
</tr>
<tr>
<td>(2) Concentration</td>
<td>Total 5 wt%</td>
</tr>
<tr>
<td></td>
<td>Ultrafine silica particle 2.5 wt%</td>
</tr>
<tr>
<td></td>
<td>Large silica particle 2.5 wt%</td>
</tr>
<tr>
<td>(3) pH</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 3.1 Schematic of TEM samples preparation

The hybrid fine particles
The hybrid fine particles

3.3. Characteristics of hybrid fine particles

The dashed lines in Figure. 3.2 show the diameters of the ultrafine and large silica particles as measured by DLS before mixing. The continuous lines represent the diameters of the large silica particles after mixing with the ultrafine colloidal silica particles. The peaks of the large particles after mixing shifted to values about 5–10 nm larger than those before mixing, while the peaks of the ultrafine particles disappeared after mixing.

Figures 3.3(a), 3.4(a), and 3.5(a) show the TEM images of silica particles with sizes of 20, 55, and 105 nm, obtained before mixing with ultrafine silica particles. The fine silica particles were almost round, uniform, well distributed, and monodispersed. However, we found that the ultrafine silica particles adhered to the surface of large silica particles and increased the diameter size of large silica after mixing process. In addition, the adherence of ultrafine silica particles on the surface of the large silica particles, changed the surface conditions of the hybrid fine particles. The remaining ultrafine silica particles that do not adhered to the surface of the large silica particle, dispersed around the hybrid fine particles as shown in Figures 3.3(b), 3.4(b), and 3.5(b).

TEM results revealed that the ultrafine silica particles adhered to the surface of large silica particles. These phenomena might be caused by disrupts the balanced net force, which is a combination of an attractive and a repulsive force between the particles as Lee et al. reported [81]. In addition, based on DLS results, we predicted that the large silica particles were coated by an approximate one layer of ultrafine silica particles. This might be the reason, which increased the size and changed the surface condition of hybrid fine particles after mixing process. The assumption of occurring the hybrid fine particles as shown in Figure 3.6.
Figure 3.2 Increase in silica particle size after mixing with ultrafine silica particle at pH 11.
The hybrid fine particles

Figure 3.3 Transmission electron micrographs of silica particles size of 20 nm
(a) before, (b) after mixing with 4 nm ultrafine silica particles

Figure 3.4 Transmission electron micrographs of silica particles size of 55 nm
(a) before, (b) after mixing with 4 nm ultrafine silica particles
The hybrid fine particles

Figure 3.5 Transmission electron micrographs of silica particles size of 105 nm

(a) before, (b) after mixing with 4 nm ultrafine silica particles.
The hybrid fine particles

Figure 3.6 Supposed model of hybrid fine particles.


The hybrid fine particles

3.4 Summary

In this study, the hybrid fine particle comprised by ultrafine silica particles and the larger silica particles sizes of 20 nm, 55 nm, and 105 nm, were studied. We found that the larger silica particles were coated by ultrafine silica particles, thereby changed the surface condition and increased the diameter size of hybrid fine particles, which were observed by TEM and DLS.
Chapter 4

Performance of hybrid fine particles

4.1 Introduction

To verify and realize the very high removal rate and very smooth planar surface without subsurface damage of sapphire wafer. In this chapter, the hybrid fine particles will be used as abrasive in sapphire CMP. The experiment results obtained using the hybrid fine particles will be compared with the conventional silica particles. In addition, the effects of hybrid fine particles in sapphire polishing was also be investigated.

4.2 Polishing tests

The polishing experiments were conducted by using a CMP machine as explained in Sect. 2.2.1. The conditions for these experiments are shown in Table 4.1. The material removal rates of sapphire were calculated by considering the wafer loss weights before and after CMP. The weight of sapphire wafers was measured using an electronic balance (A&D BM-20). The surface roughnesses of the sapphire substrates were measured by atomic force microscopy (AFM; SII SPA300HV) before and after polishing.
4.3 Material removal rates of sapphire obtained using hybrid fine particles

Figure 4.1 shows, at the same slurry contents for the hybrid (2.5 mass\% each of the ultrafine and large silica slurries, giving a total of 5 mass \%) fine particles and single-sized (5 mass \%) silica particles, we found that the former abrasives gave larger MRRs for sapphire. The MRRs of sapphire obtained by mixing ultrafine silica particles into silica slurries with particle sizes of 20, 55, and 105 nm increased by about 85, 78, and 32\%, respectively. These results revealed a synergistic effect, in which the very small silica particles may serve to facilitate a chemical reaction between the silica particles in the slurry and the alumina component of the sapphire substrate to give an alumina silicate product layer that is softer than
Performance of hybrid fine particles

Silica [66-69] and can be more readily removed by abrasion by the larger silica particles. Furthermore, the surface shape of the hybrid fine abrasive might benefit the adherence of alumina silicate on the sapphire substrate, which is caused by mechanical abrasion, as explained in Sect. 4.5.2.

4.4 Surface roughness of sapphire wafer after polishing

Figure 4.2 shows the surface roughness of sapphire before and after the polishing process. These results show that the RMS surface roughness obtained using single-sized silica gradually increased from 0.17 to 0.3 nm with the increase in abrasive size from 4 to 105 nm. This phenomenon indicated that the abrasive size influenced the surface roughness of the substrate during polishing [63]; however, the surface of the polished sapphire obtained using the hybrid fine slurries produced was smoother than that from the single-sized silica slurries. The RMS values decreased from 0.2, 0.24, and 0.3 nm to 0.14, 0.15, and 0.2 nm when using hybrid fine particles sizes of 20, 55, and 105 nm in combination with the 4 nm ultrafine silica particles, respectively. These results show that the ultrafine silica played an important role in improving the sapphire surface during CMP. We observed that the surface area of hybrid fine particles was much rougher than single-sized silica particles. These conditions might increase the coefficient of friction between the hybrid fine particles and sapphire surface during polishing process. Therefore, the material removal rates of sapphire were increased.
Performance of hybrid fine particles

Figure 4.1 MRRs of sapphire after 3 h of polishing using single-sized silica and hybrid fine particles.

Figure 4.2 Surface roughnesses of polished sapphire using single-sized silica and hybrid fine particles.
4.5 Investigation of material removal by hybrid fine particles

The polishing results by using the hybrid fine particles exhibited that the performance of sapphire CMP was improved. However, the mechanism of material removal by hybrid fine particles is still unclarified. We expect that the performance of sapphire CMP was increased by the changed in mechanical and chemical factors of hybrid fine particles. Therefore, the effects of the adherence of ultrafine silica particles on hybrid fine particles were studied. The coefficient of frictions between the sapphire substrate, polishing pad and abrasive were measured. After that, the effect of ultrafine silica particles performed mainly as the chemical factor in hybrid fine particles was also investigated.

4.5.1 Measurement of coefficient of friction

The coefficients of friction (COFs) between the sapphire substrate, abrasive particle, and polishing pad were measured using the apparatus shown in Figure 4.3. The slurry was placed, without it spreading, on the center of the polishing pad at the top of the ramp and allowed to flow down to the slurry container. We then tracked the time from which the sapphire wafer and polishing head were released at the top of the ramp until it reached the stopper. We calculated the COF from fundamentals of physics using

\[ f = \mu N \]  \hspace{1cm} (4.1)

where \( f \) is the friction force, \( \mu \) is the coefficient of friction, and \( N \) is normal force or force perpendicular to the contacting surfaces. This equation can be rewritten to define the COF for these specific conditions as expressed by Eq.

\[ \mu = \frac{gt \sin \theta - 2s}{gt^2 \cos \theta} \]  \hspace{1cm} (4.2)

where \( g \) is gravitational acceleration, \( s \) is displacement, \( t \) is time and \( \theta \) is the angle of the ramp.
Figure 4.3 (a) Schematic and (b) photograph of experimental setup for measurement of coefficient of friction.
4.5.2 The relation of MRR of sapphire and COF by hybrid fine particles

To explain the effect of hybrid fine particles on mechanical abrasion, Figure 4.4 shows the results of COF measurements. This reveals that the COF of the ultrafine silica particles was higher than those of the larger silica particles. This may be attributed to the higher probability of a slurry containing ultrafine colloidal particles producing a reacted alumina layer than that of the larger silica particles alone. In addition, we can see an almost linear correlation between the MRR of sapphire and the COF of hybrid fine particles and that the COF increased by 8–15% after mixing with ultrafine silica particles. These results confirmed that the ultrafine particles adhered to the surfaces of the larger particles in the hybrid slurry and thereby changed their shape and gave a higher surface roughness than that before mixing. In addition, a chemical effect was induced by the reaction of the ultrafine particles adhering to the surfaces of the larger particles that produced an alumina layer on the sapphire substrate. These might be the reasons why the hybrid fine abrasives exhibited larger COFs and produced higher MRRs than those of the single-sized silica slurries.
Figure 4.4 MRR of sapphire as a function of coefficient of friction.
4.5.3 Study on the effects of ultrafine silica particles substitute as the chemical factor in hybrid fine particles

In order to investigate that the chemical reactivity of hybrid fine particles was promoted by the ultrafine silica particles, the mixed fine silica particles and diamond particles were prepared as soft and hard abrasive respectively because we found that the ultrafine silica particles have a much higher chemical reactivity than the large silica particles in sapphire CMP as explained in Sect 2.3. In contrast, we found that the diamond particles exhibited that chemically inert with sapphire. We predicted that the chemical reactivity of ultrafine silica particles might promote the reacted layer on the sapphire surface and increase the material removal rate.

Preparation of mixed soft and hard abrasives

Ultrafine silica particles size of 4 nm (NALCO 1115) was used as soft abrasive and substitute chemical factor. In addition, monocrystalline diamond slurry with particles size of 100 nm (Hyperz 1/10-STD-MA S-4889) was used as hard abrasive and substitute for mechanical factor in sapphire CMP owing to the diameter size of abrasive particle in the slurry for CMP process is usually between 10-100 nm [62]. In this study, both silica and diamond slurries were mixed at different ratios. Furthermore, the single-sized silica slurries with particles sizes of 4 nm and 100 nm (NALCO 2329 Plus), and pure monocrystalline diamond slurry with particles size of 100 nm were also prepared. All prepared slurries have a details as shown in Table 4.2.
Polishing experiments using the mixed soft and hard abrasives

The polishing experiments were performed by using a CMP machine with a reuse slurry system without a filter as explained in Sect. 2.2.1. The conditions for these experiments are shown in Table 4.3. The MRR of sapphire were calculated by considering the wafer loss weights before and after CMP. The MRR was calculated by considering the sapphire wafer mass before and after CMP, measured using an electronic balance (A&D BM-20).

Table 4.2 Properties of single-sized and mixed abrasive slurries

<table>
<thead>
<tr>
<th></th>
<th>Single-sized slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>5 wt%</td>
</tr>
<tr>
<td>pH</td>
<td>11 (KOH or H₂SO₄)</td>
</tr>
<tr>
<td></td>
<td>Mixed abrasive slurry</td>
</tr>
<tr>
<td>Weight ratio</td>
<td>20:1, 10:1, 1:1, 1:10, and 1:20</td>
</tr>
<tr>
<td>pH</td>
<td>11 (KOH or H₂SO₄)</td>
</tr>
</tbody>
</table>
**Table 4.3 Polishing conditions.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wafer type</td>
<td>Sapphire</td>
</tr>
<tr>
<td>Wafer size</td>
<td>mm 25.4 × 1</td>
</tr>
<tr>
<td>Polishing pad</td>
<td>Suba 600</td>
</tr>
<tr>
<td>Polishing time</td>
<td>min 180</td>
</tr>
<tr>
<td>Polishing pad seasoning</td>
<td>Nylon brushing</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>min 5</td>
</tr>
<tr>
<td>Polishing pressure</td>
<td>MPa 0.1</td>
</tr>
<tr>
<td>Platen/carrier speed</td>
<td>rpm 60/60</td>
</tr>
<tr>
<td>Slurry amount</td>
<td>kg 0.3</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>ml/min 60</td>
</tr>
</tbody>
</table>

**MRRs of sapphire obtained using single-sized of silica particles and monocrytalline diamond particles**

Figure 4.5 shows that the MRR of sapphire obtained using colloidal silica and monocrytalline diamond slurries. These results reveal that the 100 nm diamond slurry could produce MRR of sapphire lower than obtained using 100 nm silica slurry. This could be explained that silica particle have a chemical reactivity with alumina element on sapphire surface and generate reacted alumina layer (alumina silicate), which this layer is softer than silica particle and can be removed from the sapphire surface during both sliding and rolling silica particles action on wafer but the diamond particle exhibit the pure mechanical action on sapphire surface during polishing. Therefore, we could see that the chemical reactivity between silica particle and sapphire surface enhance the performance of sapphire CMP.
Figure 4.5 Material removal rates obtained using diamond and silica particles size of 100 nm.
Performance of hybrid fine particles

MRRs of sapphire obtained using mixed soft and hard abrasive

Figure 4.6 shows that the MRR obtained using the mixed soft and hard abrasive slurry. This graph were divided into three regions. The first region show the MRR slight vacillate from 0.30, 0.29, and 0.28 μm/h at the mixing ratios (silica and diamond) of 20:1, 10:1, and 1:1 respectively. The tendency of material removal rate rather be constant value close to silica slurry size of 4 nm performed. It seem that the diamond particle in the mixed abrasive slurry do not participate in polishing process due to the number of diamond particle is much smaller than that the number of silica particle. These results implied that the obtained MRR depend on the chemical reactivity as a dominant factor. The second region explored that the MRR obtained using the mixed abrasive slurries with the mixing ratios in this region produced is larger than that obtained using 100 nm diamond slurry, especially the MRR obtained using the mixed abrasive slurry with the mixing ratio of 1:20 produced is much higher than that obtained using silica slurry sizes of 4 nm and 100 nm. These results confirmed that the effect of chemical reactivity through the silica particle in the mixed abrasive slurry promote the reacted layer in CMP process.

Furthermore, our previous results demonstrate that a small silica particle exhibit a smaller mechanical effect than that larger silica particle as explained in Sect. 2.3. Thus, ultrafine silica particle size of 4 nm could be used as substitute chemical factor in mixed silica and diamond slurry, although silica particle reveals both mechanical and chemical factors. In addition, we observed that the obtained MRR gradually increases as linear proportion from 0.28 to 0.35 μm/h from the changed of mixing ratios of 1:1 to 1:20 respectively. MRR obtained in this region might be caused by the number of diamond particle gradually increase (mechanical factor changed) but the number of silica particle gradually decrease (chemical factors changed). Therefore, these results as mentioned above reveal that both mechanical and
Performance of hybrid fine particles

chemical factors are dominant factor to produce the MRR. The last region explore that the MRR obtained using diamond slurry with particle size of 100 nm. The obtained results might be caused by pure mechanical action because no silica particle participate in polishing process. The effect of chemical reactivity produced by the silica particles (as chemical factor) as shown in Figure 4.7.
Performance of hybrid fine particles

Figure 4.6 MRRs of sapphire obtained using mixed soft and hard abrasive in slurry at different mixing ratios.
Performance of hybrid fine particles

(a) Diamond particles

(b) Mixed silica and diamond particles

Figure 4.7 Supposed mechanism of material removal by mixed soft and hard particles.
Performance of hybrid fine particles

The effect of chemical factor through the ultrafine silica particles

The polishing results obtained using the mixed soft and hard particles in sapphire CMP. We found as the following

(1) Polishing results obtained using the mixed soft and hard particles indicated that the chemical reactivity through the ultrafine silica particle enhance the performance of sapphire CMP.

(2) Ultrafine silica particles size of 4 nm perform mainly in chemical factor in mixed diamond and silica slurry.

4.6 Summary

The hybrid fine particle comprised by ultrafine silica particles size of 4 nm and the larger silica particles sizes of 20 nm, 55 nm, and 105 nm. Our study exhibited following

(1) The hybrid fine particles gave higher MRRs for sapphire CMP and smoother surface roughness than single-sized silica slurries.

(2) The contact area between the sapphire substrate and hybrid fine particles might be modified by the ultrafine silica particles adhered to the surface of larger silica particles and increased the COF of the resulting hybrid fine abrasive.

(3) Ultrafine silica particle with size of 4 nm play the role of chemical factor in sapphire CMP.
Chapter 5

Performance optimization of hybrid fine particles

In this study, to develop the performance of sapphire CMP, the hybrid fine abrasive was optimized. Based on the method for preparation of hybrid fine particles, we suppose that the performance of sapphire CMP using hybrid fine particles can be designed by adjusting the initial parameters of hybrid fine particles as following

1) The diameter sizes of large particles
2) The reactivity
3) The surface condition

The concept to study the preparation of hybrid fine particles as shown in Figure 5.1. Therefore, the optimization of the mixing ratios of hybrid fine particles is conducted by adjusting a pH value in ranges of 7-13, diameter size of large silica particles (20 nm, 55 nm, and 105 nm), and concentration of both larger and ultrafine silica particles.
Performance optimization of hybrid fine particles

Figure 5.1 Conceptual design of hybrid fine particles.
5.1 Selectivity of pH value

To improve and realize a high removal rate and very smooth surface without subsurface damage, the hybrid fine particles as abrasive in the slurry for the CMP of sapphire were studied. The hybrid fine particles were comprised by a different sizes of fine silica particles with the ranges of pH 7-13. We predict that an appropriate pH value of hybrid fine particles might affect to the aggregation of abrasive particles in a slurry and produce a higher MRR than the conventional silica slurry.

5.1.1 Preparation of hybrid fine particles

The hybrid fine particles slurries comprised 4 nm silica slurry (NALCO 1115) as the ultrafine silica particles mixed with 20 nm (NALCO 1040), 55 nm (NALCO TX15582), or 105 nm (NALCO 2329 Plus) silica slurries as the large silica particles. Details of the prepared slurries are shown in Table 5.1. The slurries were adjusted a pH by the addition of either KOH or H₂SO₄, as appropriate. The sizes of the fine silica abrasives were measured before and after mixing by dynamic light scattering (DLS; Malvern ZETASIZER Nano S).

5.1.2 Polishing tests

The polishing experiments were conducted by using a CMP machine as explained in Sect. 2.2.1. The conditions for these experiments are shown in Table 5.2. The material removal rates of sapphire were calculated by considering the wafer loss weights before and after CMP. The weight of sapphire wafers was measured using an electronic balance (A&D BM-20).
Performance optimization of hybrid fine particles

Table 5.1 Properties of hybrid fine particles as abrasive.

<table>
<thead>
<tr>
<th>(1) Diameters of fine particle</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.1) Ultrafine silica particle</td>
<td>4 nm</td>
</tr>
<tr>
<td>(1.2) Large silica particle</td>
<td>20, 55, and 105 nm</td>
</tr>
<tr>
<td>(2) Concentration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total 5 wt%</td>
</tr>
<tr>
<td></td>
<td>Ultrafine silica particle 2.5 wt%</td>
</tr>
<tr>
<td></td>
<td>Large silica particle 2.5 wt%</td>
</tr>
<tr>
<td>(3) pH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7-13</td>
</tr>
</tbody>
</table>

Table 5.2 Polishing conditions.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>mm</th>
<th>Sapphire (Al$_2$O$_3$) φ 25.4, t = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polishing pad</td>
<td></td>
<td>Suba600</td>
</tr>
<tr>
<td>Polishing time</td>
<td>min</td>
<td>60</td>
</tr>
<tr>
<td>Polishing pad seasoning</td>
<td></td>
<td>Nylon brushing</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>min</td>
<td>5</td>
</tr>
<tr>
<td>Polishing pressure</td>
<td>MPa</td>
<td>0.1</td>
</tr>
<tr>
<td>Platen/Carrier</td>
<td>rpm</td>
<td>60/60</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>ml/min</td>
<td>60</td>
</tr>
<tr>
<td>Number of sample</td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>
5.2 Results and discussion

5.2.1 The diameter size of hybrid fine particles

Figure 5.2 shows the increase in diameter sizes of hybrid fine particles after mixing with the ultrafine silica particles depended on the pH value. The results revealed that the abrasive size gradually increased with increasing of pH values from pH 7 and reached the maximum size at pH 11. After that, the diameter size of hybrid fine particles slightly decreased at the pH 13.

These results might be caused by the silica particles were covered by a many silanol groups (SiOH) and hydroxyl groups (OH) [82]. Figure 5.3 shows the silica particle sizes is sharply increased as a function of the concentration of hydroxyl groups according to the stability of the fine silica as shown in Figure 5.4. The silica particles is in the range of particle growth from pH 7 – 11, and approach to dissolves when above approximately pH 11. These might be the reasons why the diameter size of hybrid fine abrasives decreased at pH 13.
Figure 5.2 The increase in size of hybrid fine particles depended on pH values.
Performance optimization of hybrid fine particles

Figure 5.3 Increase in silica particle size as function of hydroxyl group concentration.
Performance optimization of hybrid fine particles

Figure 5.4 Increase in silica particle size as function of hydroxyl group [82-83].
Performance optimization of hybrid fine particles

5.2.2 MRR of sapphire variant by pH values of hybrid fine slurries

Figure 5.5 shows the material removal rates of sapphire obtained by using hybrid fine particles sizes of 4 nm and 20 nm is smaller than that hybrid fine particles sizes of 4 nm in combination with the silica particle sizes of 105 and 55 nm respectively. In addition, these graphs exhibited that the MRRs of sapphire obtained using hybrid fine particles size of 20 and 4 nm as abrasive in the slurries increase with increasing of pH 7 to pH 13 respectively. On the other hand, the hybrid fine particles sizes of 4 nm in combination with the silica particles sizes of 55 and 105 nm respectively, reached the maximum MRRs of sapphire at pH 11 and decrease to smaller MRR at pH 13.

In these case, the MRRs of sapphire obtained by using hybrid fine particles might depend on the abrasive size (mechanical factor) that depended on pH values. However, we found that at pH 13, the main factor of hybrid fine particles sizes of 20 nm and 4 nm might be the chemical reactivity because the abrasive size (mechanical factor) at pH 13 is smaller than that at pH 11.

5.3 The condition of proper pH

Based on the results of diameter size and material removal rates obtained using the hybrid fine particles with ranges of pH 7-13. These results illustrated that the appropriate condition of pH value, which appropriate to accumulate the small and large silica particle in each kinds of slurry is pH 11.
Figure 5.5 MRRs of sapphire depend on pH value after polishing time of 1 h.
5.4 Optimization of mixing ratio of hybrid fine particles

The hybrid fine particles (HP) were optimized by varying the mixing ratio, or the concentration of ultrafine silica particles (US) and large silica particles (LS) in the slurry as shown in Table 5.3. The polishing experiments and polishing conditions for these experiments as shown in Sect. 4.2.

The characteristics of hybrid fine particles were observed by transmission electron microscopy (TEM; FEI Tecnai G2 Spirit; accelerating voltage: 120 kV) both before and after polishing process. The silica samples were prepared by the same method as explained in Sect. 3.2.

Table 5.3 Properties of hybrid fine particles for optimization

<table>
<thead>
<tr>
<th>(1) Size of fine particle</th>
<th>Total 5 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.1) US particle</td>
<td>4 nm</td>
</tr>
<tr>
<td>(1.2) LS particle</td>
<td>20, 55, and 105 nm</td>
</tr>
<tr>
<td>(2) Concentration</td>
<td>Total 5 wt%</td>
</tr>
<tr>
<td>(weight ratio of the large silica to ultrafine silica in a slurry, LS:US)</td>
<td></td>
</tr>
<tr>
<td>(A) 1:30</td>
<td>LS : 0.17 wt%, US : 4.83 wt%</td>
</tr>
<tr>
<td>(B) 1:20</td>
<td>LS : 0.24 wt%, US : 4.76 wt%</td>
</tr>
<tr>
<td>(C) 1:10</td>
<td>LS : 0.50 wt%, US : 4.50 wt%</td>
</tr>
<tr>
<td>(D) 01:1</td>
<td>LS : 2.50 wt%, US : 2.50 wt%</td>
</tr>
<tr>
<td>(E) 10:1</td>
<td>LS : 4.50 wt%, US : 0.50 wt%</td>
</tr>
<tr>
<td>(F) 20:1</td>
<td>LS : 4.76 wt%, US : 0.24 wt%</td>
</tr>
<tr>
<td>(G) 30:1</td>
<td>LS : 4.83 wt%, US : 0.17 wt%</td>
</tr>
<tr>
<td>(3) pH</td>
<td>11</td>
</tr>
</tbody>
</table>
5.4.1 MRR of sapphire using hybrid slurries with different mixing ratios

Figure 5.6 shows the material removal rates of sapphire obtained using hybrid fine particles at the different mixing ratios. These results revealed that the MRR of sapphire obtained by mixing the ultrafine silica particles size of 4 nm into 105 nm silica slurry, was higher than that obtained by mixing the ultrafine silica particles size of 4 nm into silica slurries with sizes of 55 nm and 20 nm respectively. The MRRs for hybrid fine particles comprised by 105 nm and 4 nm gradually increases from 0.34 to 0.42 μm/h from the mixing ratios of 1:30 to 10:1 respectively. After that, the MRR sharply decreases to 0.32 μm/h at the mixing ratio of 30:1. In the case of hybrid fine particles comprised by 55 nm and 4 nm, the MRR of sapphire gradually increases from 0.29 to 0.35 μm/h from the mixing ratios of 1:30 to 1:1 respectively. Then, the MRR decreases to 0.27 μm/h at the mixing ratio of 30:1. A similar MRR was obtained using hybrid fine particles comprised by 20 nm and 4 nm. The MRR increases from 0.28 to 0.30 μm/h from the mixing ratios of 1:30 to 1:20 respectively and decreases to 0.16 μm/h at the mixing ratio of 30:1.

From these results, the MRRs of sapphire obtained using hybrid fine particles produced the highest MRR at the different mixing ratios and depended on the size of large silica particle. However, the highest MRR obtained using hybrid fine particles could be considered on the number ratio of the ultrafine silica to large silica in a slurry as discussion in Sect. 5.5.

5.4.2 Surface roughness of polished sapphire

The surface roughnesses (RMS) of polished sapphire using single-sized silica and hybrid fine particles as shown in Figure 5.7. These results show that the surface quality of sapphire substrate obtained using hybrid fine particles with the different mixing ratios, which produced the highest MRR, was smoother than that obtained using single-sized silica particles.
The RMS values obtained by mixing ultrafine silica particles into larger silica slurries with particle sizes of 20, 55, and 105 nm decrease from 0.20, 0.24, and 0.30 nm to 0.16, 0.15, and 0.16 nm respectively.

5.4.3 Characteristics of hybrid fine particles after polishing

Figures 5.8(a), 5.9(a), and 5.10(a) show the TEM images of hybrid fine particles comprised by large silica particles with sizes of 20, 55, and 105 nm mixed with ultrafine silica particles at mixing ratio of 1:1, obtained before polishing process. We found that the ultrafine silica particles adhered to the surface of large silica particles. The adherence of ultrafine silica particles appeared the good distribution on the surface area of larger silica particles.

However, the characteristics of hybrid fine particles were changed after polishing process. The TEM images revealed that the ultrafine silica particles still adhered to the surface of larger silica particles after polishing process but different characteristics in each types of hybrid fine particles as shown in Figures 5.8(b), 5.9(b), and 5.10(b).

The hybrid fine particles comprised by 20 nm and 4 nm exhibited that ultrafine silica particles were accumulated on the larger silica particles denser than before polishing process, while the remaining ultrafine silica and hybrid fine particles dispersed in the slurry and seem not different from before polishing. In case of hybrid fine particles comprised by 55 nm and 4 nm revealed the much different characteristics. We found that the hybrid fine particles accumulated the much layer of ultrafine silica particles as the cluster of fine particles on the surface of larger silica particles. In case of hybrid fine particles comprised by 105 nm and 4 nm showed that the characteristics of hybrid fine particles were almost same as before polishing process but the diameter size of ultrafine silica particles was larger than before polishing.
Figure 5.6 Material removal rates of sapphire obtained using hybrid fine particles with different mixing ratios.
Figure 5.7 Surface roughness of polished sapphire using the different types of slurry.
Performance optimization of hybrid fine particles

Figure 5.8 Transmission electron micrographs of hybrid fine particles comprised by 20 nm and 4 nm silica particles (a) before and (b) after polishing process

Figure 5.9 Transmission electron micrographs of hybrid fine particles comprised by 55 nm and 4 nm silica particles (a) before and (b) after polishing process
Performance optimization of hybrid fine particles

Figure 5.10 Transmission electron micrographs of hybrid fine particles comprised by 105 nm and 4 nm silica particles (a) before and (b) after polishing process
5.5 The effect of mixing ratio of hybrid fine particles on sapphire CMP

Although, the hybrid fine particles produced a higher MRRs of sapphire than the single-sized silica particles. The MRRs of sapphire obtained using hybrid fine particles with the different mixing ratios as explained in Sect. 5.4.1 exhibited that the number ratio (mixing ratio) of large silica and ultrafine silica particles into the hybrid fine particles affected to the performance of the sapphire polishing process. This might be caused by the correlation between the total number of ultrafine silica particles that adhered to the surface of large silica particles due to the remaining ultrafine silica particles that not adhered to the surface of large silica particles performed mainly in chemical factor and provided a higher reacted layer (alumina silicate) on the sapphire surface than the larger silica particles [62]. The number of ultrafine silica particles are much larger than the number of hybrid fine particles and exhibited a high possibility to contact on a sapphire surface before the hybrid fine particles remove the reacted layer as shown in Figure 5.11.

Furthermore, TEM images as shown in Sect. 5.4.3 revealed that the hybrid fine particles indicated the different mechanism of material removal might depends on the number ratio of hybrid fine particles and the diameter size of larger silica particles. Based on the polishing results and TEM images, the supposed mechanism of material removal by hybrid fine particles might be divided to three cases as shown in Figure 5.12. The description of material removal as explained as following
Figure 5.11 Supposed model of material removal by hybrid fine particles
(a) US contact to the sapphire surface (b) during US and HP contact to the sapphire surface and (c) US and HS removed reacted layer from the sapphire surface.
Figure 5.12 Supposed mechanism of (a) high mechanical and low chemical factors, (b) low mechanical and high chemical factors, and (c) the balance of chemical and mechanical factors in sapphire removal by hybrid fine particles.
Performance optimization of hybrid fine particles

Case I: High mechanical and low chemical factors

This case occurred when the number of ultrafine silica particles become small. In this case, the mechanical action by abrasive particles is higher than the chemical reaction to produce the reacted layer. Therefore, the removal rate was limited by the chemical factor.

Case II: Low mechanical and high chemical factors

This case occurred when the number of ultrafine silica particles become large. In this case, the mechanical action by abrasive particles is lower than the chemical reaction to produce the reacted layer. Therefore, the removal rate was limited by the mechanical factor.

Case III: The balance of mechanical and chemical factors

This case occurred when the number ratio of ultrafine silica particles and larger silica particles is balance. In this case, the mechanical action and the chemical reaction produce a steady state of chemical reaction rate to produce the softer layer and mechanical action to remove those reacted layer produce the reacted layer.

In addition, we found that the highest MRRs of sapphire obtained using hybrid fine particles sizes of 20, 55, and 105 nm in combination with the 4 nm ultrafine silica particles with the different mixing ratio. In this case, we found that the highest MRR of sapphire occurred at the ultrafine silica to large silica number ratio about 2,000:1. These results might be caused by the balance of mechanical and chemical factors.
5.6 Summary

In this study, the hybrid fine particles in the slurry for sapphire CMP were studied. We found as following:

(1) The performance of sapphire CMP depended on the initial parameter of hybrid fine particles in the slurry such as the pH value, the diameter size of large particles, and the mixing ratio.

(2) The mixing condition of pH 11 is appropriate value to produce the hybrid fine particles in sapphire CMP.

(3) The proper mixing ratio of ultrafine silica particles and larger silica particles produced the balance of chemical and mechanical factors in sapphire CMP and gave the higher performance of material removal rate and surface roughness of sapphire.
Chapter 6

Conclusions

The implementation of experimental methods in this research is study and improve the performance of sapphire CMP. Our content of the research comprises the study on characteristics of single-sized silica particles, the design of hybrid fine particles, considering the fabrication, characterization, and the optimization of hybrid fine particles. In addition, investigating and explaining the mechanism of material removal by hybrid fine particles were also conducted.

Chapter 1 mentioned the applications of sapphire wafer and the process to produce the very smooth and high planarized surface of sapphire wafer. Fundamental of the conventional chemical mechanical polishing (CMP) and a brief of sapphire CMP were described. The consumable costs during CMP process were also presented. The end of this chapter exhibits the issue of sapphire CMP process and the method to solve the issue was proposed.

Chapter 2 explains about the method to specify characteristics of fine silica abrasive in sapphire CMP. The change in fine particle size in slurries including its effect on the performance of the CMP technique were study. We found that sapphire is removed by adhering such a material to silica fine particles during CMP. The alumina element (alumina silicate) from sapphire coated silica fine particles. Then, MRRs decreased with increasing of polishing time owing to the degradation of particles in the slurry. Finally, the characteristics of silica particle were specified. In addition, we found that the novel characteristics of ultrafine silica particles with size of smaller than 10 nm exhibit the chemical reactivity as the dominant factor.
**Conclusions**

Chapter 3 describes the method to improve the performance of sapphire CMP by using the hybrid fine particles. The process to produce the hybrid fine particles was proposed. After that, explains about the characteristics of hybrid fine particles. The results showed that the larger silica particles were coated by ultrafine silica particles, thereby changed the surface condition and increased the diameter size of hybrid fine particles.

Chapter 4 presents the performance of hybrid fine particles in sapphire CMP. We found that the hybrid fine particles enabled a much higher performance of sapphire polishing than single-sized silica particles. After that, the investigation of higher performance of sapphire CMP by hybrid fine particles was conducted. We found that the ultrafine silica particles enhance the chemical reactivity in sapphire CMP.

Chapter 5 mentions to the optimization of mixing ratio of hybrid fine particles was conducted by adjusting a diameter size of larger silica particles and concentration of both large and ultrafine silica particles. We found that the proper condition of hybrid fine particles to produce a very high performance of sapphire CMP.

In this chapter is the conclusions that summarizes this research, we conclude that

1. The ultrafine silica particles exhibited the unique characteristics, it produced a very high material removal rate.
2. The hybrid fine slurries gave higher material removal rate for sapphire than single-sized silica slurries.
3. The ultrafine silica particles and hybrid fine particles improved the surface roughness of sapphire.
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Appendix

A.1 Publication articles


A.2 International conferences


A.3 Domestic conferences
