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Research Article

Synthesis and Characterization of SiO_2 Nanoparticles and Their Efficacy in Chemical Mechanical Polishing Steel Substrate

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Chemical mechanical polishing (CMP) technology is extensively used in the global planarization of highly value-added and large components in the aerospace industry. A nanopowder of SiO_2 was prepared by the sol-gel method and was compounded into polishing slurry for the CMP of steel substrate. The size of the SiO_2 abrasives was controlled by varying the sol-gel reaction conditions. The polishing efficacy of nano-SiO_2 was studied, and the CMP mechanism with nanosized abrasives was further investigated. The proposed methods can produce SiO_2 abrasives whose size can be controlled by varying the sol-gel reaction conditions. The size of the SiO_2 abrasives was controlled in the range from 58 to 684 nm. The roughness of the steel substrate strongly depends on the size of the abrasive, and the surface roughness decreases as the abrasive size declines. A super-smooth surface with a roughness of 8.4 nm is obtained with nanosized SiO_2. Ideal CMP slurry can be used to produce material surfaces with low roughness, excellent global planarization, high selectivity, an excellent finish, and a low-defected rate.

1. Introduction

As the requirements for precise microcomponents have increased dramatically for the last few years, finishing techniques to improve the surfaces of microstructures have attracted more attention. For example, the surface quality of microlenses critically affects the performance of an optical system. To produce glass, ceramics, and semiconductors with surfaces of superior quality, abrasive polishing is commonly required as a finishing step [1]. Chemical mechanical polishing (CMP) is a suitable method for smoothing the surface. It is used in many industrial processes, including the manufacture of devices and materials. It has recently attracted much interest owing to its strong performance in terms of material removal rate (MRR) and surface quality.

Steel substrate could be applied to the surface grinding machine, slideway, air bearing, and so on. There were more and more ultraprecision machines with the use of CMP technique in order to produce steel substrate. During the CMP process, the formation and removal of the oxide layer are done repeatedly. Thakurta et al. [2] used slurry hydrodynamics, mass transport, and reaction kinetics to predict the polishing rate of a steel film. These steps include (1) mass transport of the oxidizer to the steel surface; (2) reaction of the oxidizer with steel to form a reacted layer, and (3) subsequent removal of the reacted layer by mechanical abrasion [3]. In the CMP process, the extension of surface defect formation must be minimized while good planarity and optimal material removal rates are maintained. Removing materials from films' surfaces in the CMP process is typically performed by chemical reaction and mechanical abrasion. The major process parameters of CMP are slurry, polishing pressure, and polishing pad. In CMP, the abrasive critically affects the quality of the polished surface. Its properties, including type, size, shape, and concentration of particles, significantly affect CMP performance. Presently, alumina, silica, and ceria are extensively used in CMP slurries as traditional inorganic abrasives [4, 5].

One of the most critical problems is the high cost of consumables (COC), such as the pad and slurry, which are responsible for over 70% of cost of ownership (COO). Since enough slurry is required to yield a high removal rate and low nonuniformity, the purchase of slurry is responsible for approximately half of the COC for a typical CMP process. Silica (SiO_2) is used in CMP slurry because it has relatively significant advantages. It can be easily prepared as monodispersed spheres by the sol-gel method and the preparation cost is low.

Nanoparticles have attracted much interest in recent years due to their excellent physical and chemical properties. They are different from conventional bulk materials in their extremely small size and larger specific area of surface. The preparation and applications of nanoparticles for adding in slurry have become important fields of research. Nanoparticles have been prepared by precipitation, solvothermal methods, radiolytic methods, electrochemical methods, chemical reduction, plasma, chemical vapor deposition, and the sol-gel method. Of these approaches, the sol-gel method is particularly useful. Its advantages are effective stoichiometric control and the production of ultrafine particles with a narrow size distribution in relatively short processing time at low temperatures.

SiO_2 nanoparticles have particular physical, chemical, and optical properties that have led to its wide use in many fields. They are used as functional materials, catalyst, plastics, rubbers paints, biomedicine, and semiconductive material. High-quality SiO_2 nanoparticles cannot be produced by conventional methods. The sol-gel approach is one of the most important methods for preparing high-quality nano-SiO_2 powders [6].

The colloidal silica of monodispersed sizes is commonly synthesized by the Stöber et al. [7] process by hydrolysis and the condensation of TEOS precursors in an alcoholic medium, catalyzed by ammonia or acid. In this work, SiO_2 particles of uniformly distributed sizes were synthesized by the sol-gel method. The obtained SiO_2 particles have many advantages, including narrow size distribution and desirable characteristics, such as very small size, high chemical purity, and high chemical homogeneity. However, this method has rarely been applied to synthesize SiO_2 abrasives for CMP slurry [8].

According to Seo and Lee [9], the polishing mechanism in the CMP process involves repeated passive layer formation by the oxidizer and abrasion by the abrasives in the slurry. However, balanced etching and passivation reactions are required to avoid a high etching rate and to ensure a high global surface planarity. Larsen-Basse and Liang [10] reviewed the fundamental mechanisms of the material removal in lapping and polishing processes and identified key areas where further work is required. Zhang and Lei [11] discussed material removal mechanisms in the finishing of advanced ceramics and glasses. To improve planarization in the CMP process, the nature of the contact between the abrasive and the oxide layer must be understood in detail, and the effect of the abrasive slurry studied. Understanding the effect of an oxidizer on the metal passivation film is important to increase the removal rate and achieve a very low nonuniformity. Future optimization of CMP metal patterning will require a deeper understanding of the mechanisms of material removal during polishing [11, 12].

Xie and Bhushan [13] provided a theoretical model, based on the abrasion mechanism, to predict the effects of particle size, the polishing pad, and the contact pressure during the CMP process. Luo and Dornfeld [14] took a step toward determining the effect of the distribution of sizes of abrasives on the surface roughness of material in CMP. The main cause of microscratches is reportedly very large particles in the slurry. A CMP experiment conducted by Basim et al. [15] revealed that the frequency of microscratches increased with the size and the number of the largest abrasive particles. Zhong et al. [16] observed that the density of the microscratches increased with polishing pressure and their size increased with the abrasive particles. Mechanical abrasion by the sliding indentation of abrasive particles is believed to be the main cause of microscratching [1].

Presently, larger abrasives are typically used in the polishing of silicon wafers, commonly damaging their surfaces severely and causing CMP to create a polishing haze. The main problems in the final CMP processes include surface scoring, a polishing haze, and contamination by metal ions and residual particles. Smaller abrasions are usually recognized to produce surfaces with better finishes. No conclusive results have been obtained concerning the effect of the abrasive particle size on the roughness of CMP material. In this work, single crystalline SiO_2 particles with various mean sizes were synthesized by the sol-gel method. Therefore, the effects of polishing on the average roughness (Ra) of the surface were studied in a steel substrate that had undergone CMP with the prepared SiO_2 nanoparticles abrasives.

2. Experimental Procedure

2.1. Materials. The formation of SiO_2 nanoparticles via sol-gel approaches was studied (Lindberg et al. [6]; Satoh et al. [17]; Zhao et al. [18]). A precursor solution was prepared from tetraethyl orthosilicate (TEOS: $Si(OC_2H_5)_4$, technical grade, 97%); ethanol (95%) was adopted as the solvent of the precursor. Ammonia (NH_3, 28%) solution was used to increase the pH to promote gelation. H_2O was distilled and underwent ion-exchange. All reagents were used without further purification. The workpieces were made of steel disk substrates (AISI 52100 steel; composition: 0.95–1.05% C, 0.15–0.35% Si, 0.2–0.4% Mn, <0.027% P, <0.020% S, 1.3–1.65% Cr, <0.3% Ni, and <0.25% Cu), containing surface hardness of 60–62 HRC. The surface average roughness (Ra) of disk substrates before polishing is around Ra = 0.1 μm. A commercial polishing pad was made by Sense Tek Co., Ltd. Taiwan; Table 1 presents its physical properties.

2.2. Preparation of SiO_2 Nanoparticles. The SiO_2 nanoparticles were prepared by the following procedure. Solution A was a mixture of TEOS (0.025–0.3 mol) and ethanol (0.25–1.5 mol). Solution B was a mixture of NH_3 (0.1–0.75 mol), H_2O (0.25–2.0 mol), and ethanol (0.25–1.5 mol). Solutions A and B were then mixed together with vigorous stirring

Table 1: Physical properties of the pad supplier.

Thickness (mm)	1.2
Weight (g/m^2)	350
Density (g/m^3)	0.40
Compressibility (%)	8.5
Elasticity (%)	82
Pore size (μm)	40

for 30 min. The final mixture was dried at 80°C for 6 hours and calcined for 24 hours at 120°C. Finally, different sizes of SiO_2 nanoparticles were obtained. Figure 1 presents the procedure for synthesizing SiO_2 nanoparticle. The particle size distribution of the SiO_2 nanoparticles was measured by using a laser particle size analyzer.

2.3. Preparation of Slurries for CMP. To study the CMP performance of the synthesized SiO_2 abrasives, a polishing test was performed using six slurries with different sized abrasives. The polishing slurries were prepared with nanosized SiO_2 powder and DI water. SiO_2 particles were added to DI water in a container with continuous stirring. This mixed slurry was sufficiently dispersed by using a stirrer before polishing to prevent aging and the precipitation of the mixed slurry. H_2O_2 as an oxidizer was used. Ultrasound was used to disperse the oxidizer in the slurry. After the pH value was adjusted to between three and four by adding NaOH, the mixture was milled for one hour in a vibrator that contained ZrO_2 balls. Then, the mixture was filtered with a 1 μm pore filter. The baseline slurry was used to compare the relative polishing performance of the slurries developed in this study.

2.4. Polishing Tests. Figure 2 schematically depicts a typical CMP process. Before polishing, the slurry was agitated continuously with a magnetic stirrer to maintain good dispersion. The slurry was constantly fed to the center of the platen [10]. Table 2 presents the ranges of the down force, down pressure, table speed, and slurry flow rate. The polishing time in the CMP process on the polishing performance was measured.

2.5. Measurements of Polishing Material Surface Roughness. The roughness of the steel substrate was measured before and after polishing with a surface profiler. The average roughness (Ra) of the polish surface was measured to evaluate the effects of polishing in various slurries. The abrasive particles and polished samples were studied via using SEM. All of the above factors served as incentives to develop the basic understanding and the necessary tools to control the CMP process closely.

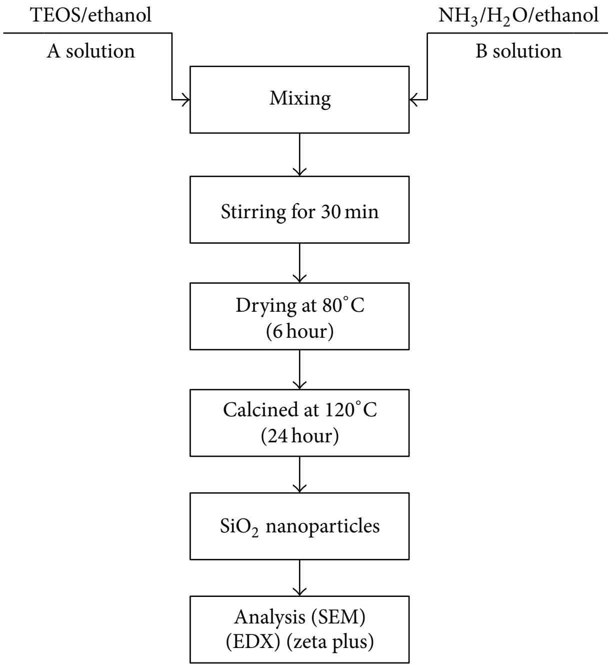


Figure 1: Experimental procedure for the synthesis of SiO_2 nanoparticles using sol-gel method.

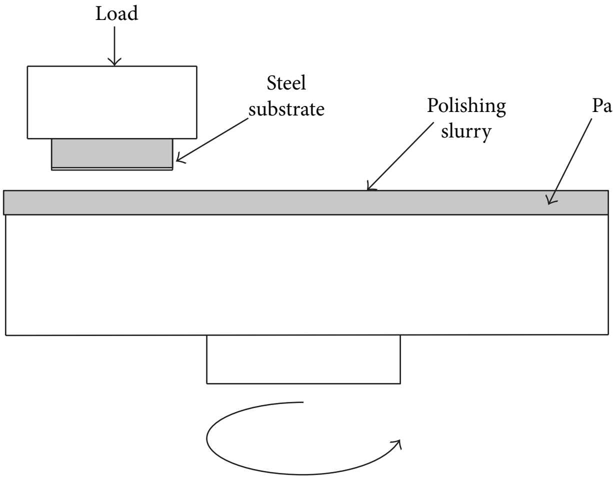


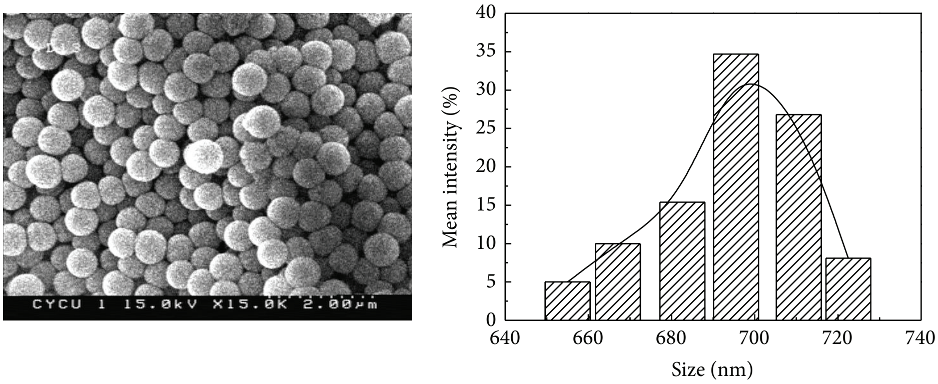
Figure 2: Schematic representation of the CMP.

Table 2: CMP test conditions.

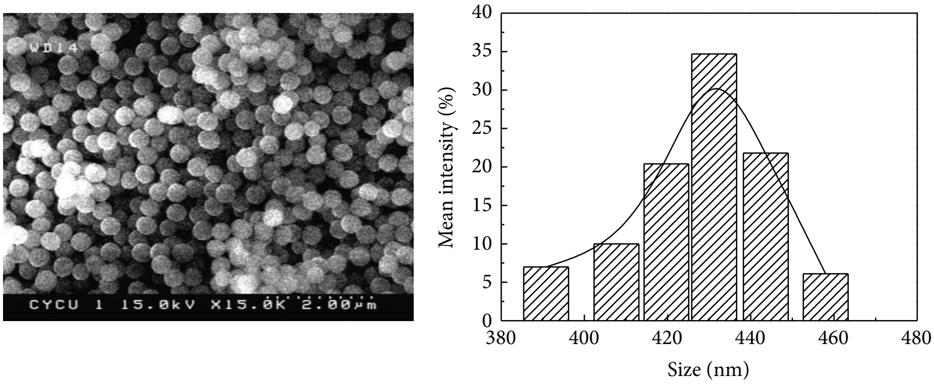
Down force (N)	20
Down pressure (N/cm^2)	0.52
Table speed (rpm)	200
Polishing time (min)	20
Slurry flow rate (mL/min)	100

3. Results and Discussion

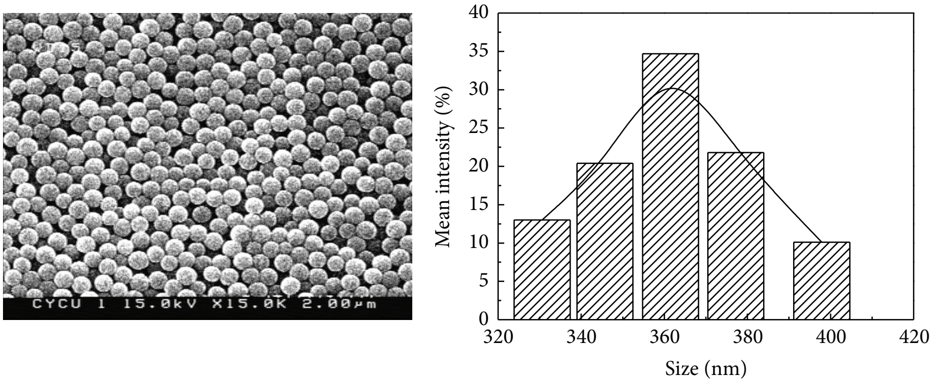
3.1. Characterization of SiO_2 Nanoparticles. Figure 3 presents the FE-SEM micrograph and particle size distribution of the SiO_2 nanoparticles obtained under different sol-gel conditions. The photograph of the SiO_2 nanoparticles indicates the uniform distribution of their sizes and their spherical shape. Figure 3 shows the distribution diagram, 684 nm, 420 nm, 362 nm, 215 nm, 140 nm, and 58 nm, which almost showed narrow size distribution. The composition of SiO_2 nanoparticles was qualitatively analyzed by EDS presented



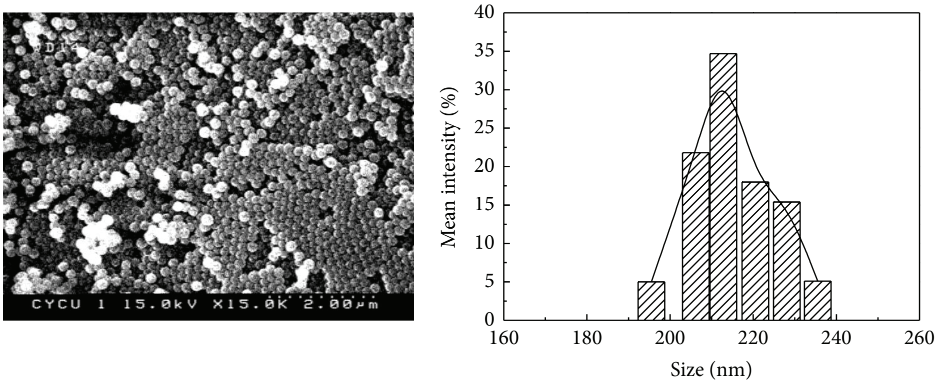
(a) 684 nm



(b) 420 nm

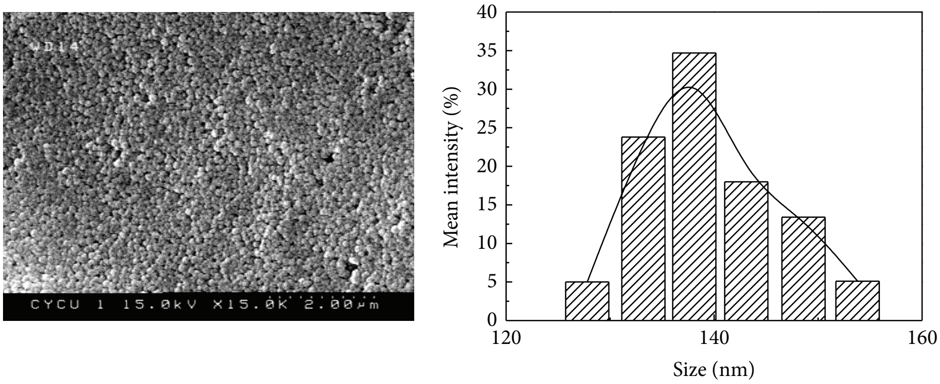


(c) 362 nm

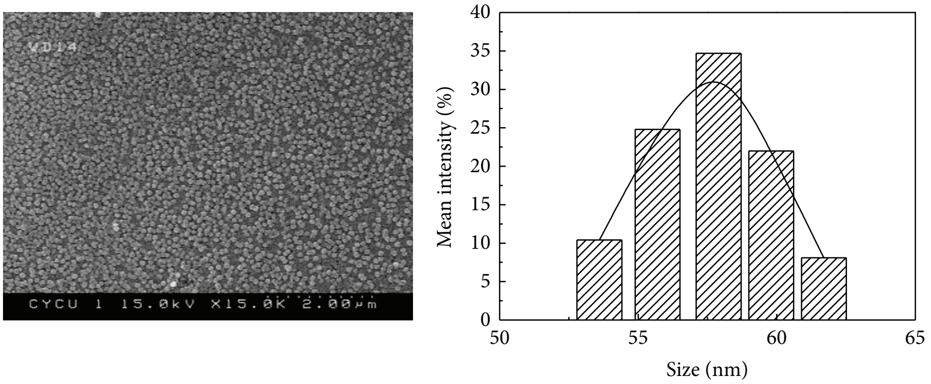


(d) 215 nm

Figure 3: Continued.



(e) 140 nm



(f) 58 nm

Figure 3: SEM micrographs and size distribution of SiO_2 nanoparticles.

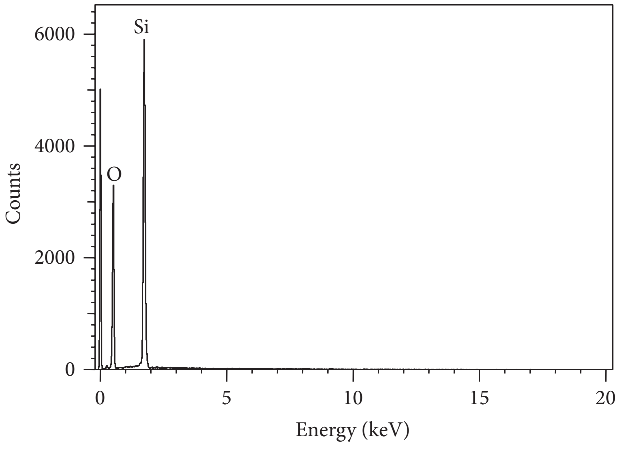


Figure 4: EDS spectrum of the SiO_2 nanoparticles.

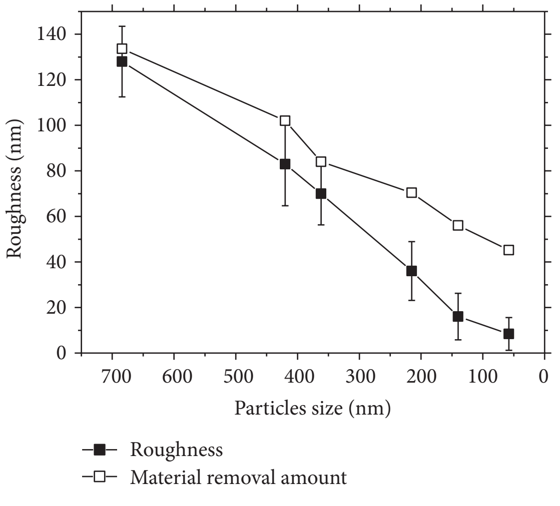
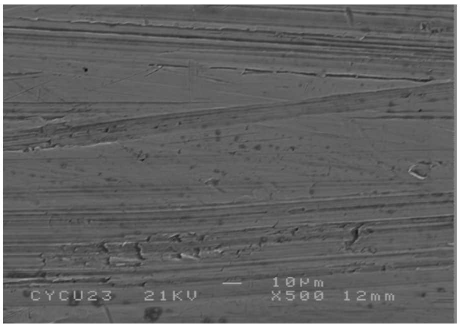


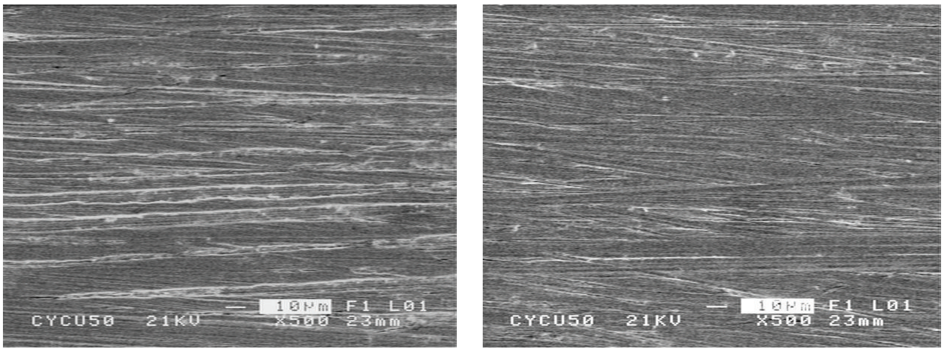
Figure 5: The roughness of steel substrates surfaces and the material removal amount with various sizes of slurries of silica particles.

in Figure 4. The nanoparticles are clearly composed of Si and O elements. No other elements were present in the SiO_2 nanoparticles. Therefore, SiO_2 nanoparticles can be effectively synthesized through the sol-gel method.

3.2. Morphology and Roughness of Polished Steel Substrate Surface. In chemical mechanical polishing of surfaces, abrasives are critical. As precisely controlled, stable distribution of particle sizes is a key contributor to maintaining low defect levels. Figure 5 presents the roughness of surfaces of steel substrates that were polished with slurries of silica particles of various sizes, dispersed in 2 wt.% H_2O_2 and DI water. The effect of the particle size on the roughness of a polished

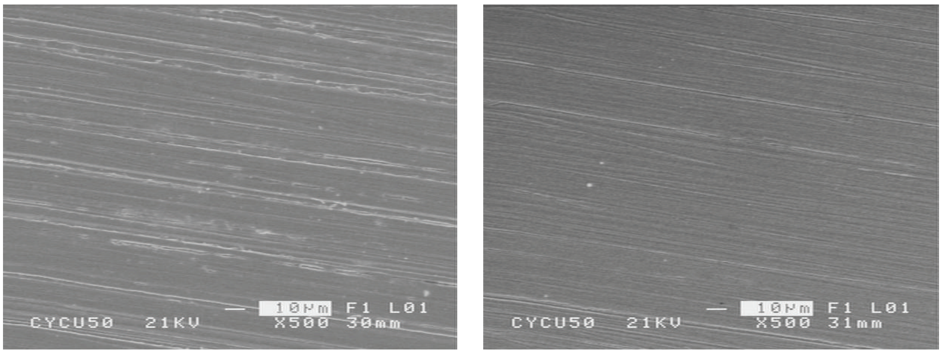


(a) Before polishing



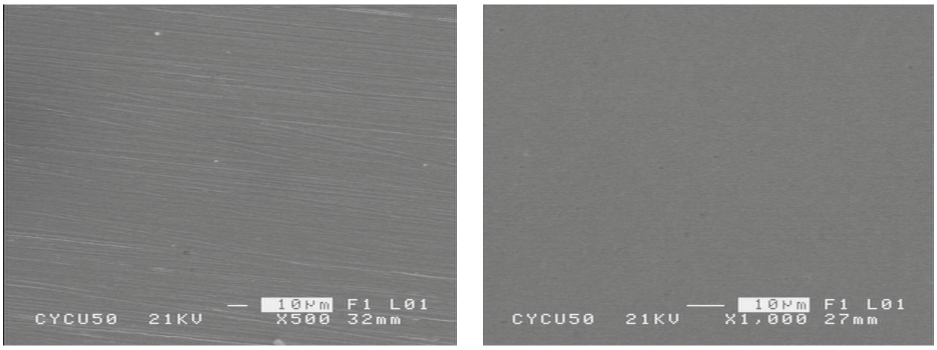
(b) 684 nm

(c) 420 nm



(d) 362 nm

(e) 215 nm



(f) 140 nm

(g) 58 nm

Figure 6: Surface profiles of steel substrates polished in different slurries.

steel substrate surface was evaluated through silica with a fixed solid content (2 wt.%) under the conditions that were specified above. Figure 5 shows that the surface roughness is 128 nm with the polished particles diameter of 684 nm and that it declined rapidly to 16 nm with 140 nm. In addition, it is 8.4 nm with up to 58 nm.

Figure 5 presents that the use of big SiO_2 particles made the roughness of steel substrate surface and the amount of removal material in CMP bigger. On the contrary, the use of small SiO_2 particles made the roughness of steel substrate surface and the amount of removal material in CMP smaller. The big SiO_2 particles possess more cutting. Cutting had a strong impact on bigger roughness of steel substrate surface as well as bigger amount of removal material. The amount of removal materials lowered down with the decreasing size of SiO_2 particle.

Large-sized SiO_2 causes larger cutting depth. The main mechanism is removal of material. Since the use of larger particles results in a more unequal distribution of the applied load on the surface of the steel substrate, it commonly results in the formation of defects. The reduction of nanosized SiO_2 particles made cutting depth decline rapidly. The reason why the material removed is plastic flowage. Finally, the smoothest surface with a roughness of 8.4 nm was obtained. [8].

The observed variation in the roughness of the polished material is attributed to two factors. (1) Indentation increases with particle size, increasing the roughness of the material, and (2) the number of particles per unit area between the substrate and the pad is reduced since the concentration is constant. Samples that are polished with slurries containing smaller particles are less rough because the indentations are shallower. Polishing with slurry that contains smaller abrasives effectively reduces microroughness and the thickness of the damaged layer that is formed by the abrasion.

3.3. Observation of Polished Surface.

Figure 6 presents typical SEM images of the steel substrate surface before and after CMP. The surface before polishing is uneven and has many a large number of scratches (Figure 6(a)). The presence of larger particles in the CMP slurry increases the defect density and surface roughness of the polished steel substrate (Figures 6(b) and 6(c)). Polishing in the slurry with small abrasives (58 nm) makes the surface much smoother (Figure 6(g)) than an unpolished one (Figure 6(a)) with no observable scratches. The surface of the steel substrate becomes uniform and flat after it is polished for a long time, and the coarseness of the original surface is eliminated.

3.4. CMP Process and Mechanism.

The CMP process involves a combination of chemical, mechanical, and hydrodynamic effects. Many models of material removal mechanisms during CMP have been proposed based on basic principles of polishing, contact mechanics, hydrodynamics, and abrasive wear mechanisms. Although there is a lack of a model of the entire CMP process, corrosion and abrasive wear may be agreed to be two basic effects of the material removal process [19].

Research reveals that CMP is a complex multiphased reaction process. It primarily involves the following two dynamics. First, the active component in the polishing slurry reacts with the atoms in the steel substrate; this step is an oxidation-reductive chemical reaction. Second, the new steel surface which is polished by slurry exposure after the resultant slowly separates from the surface. The abovementioned two steps determine the rate of material removal and completeness. Therefore, key means of influencing the two dynamic processes and related theory must be known before the degree of finishing and CMP can be effectively studied [20].

In this study, CMP reduced the uniformity of surface because the particles in the slurry that contained large abrasives had a wide size distribution. This result reveals that an optimal size of the abrasive in the slurry system that minimizes surface roughness exists. Based on the above process analysis, a new polishing mechanism that uses small abrasives, rapid reaction, and a rapid desorption is proposed. Polishing slurry with smaller abrasives yields a lower roughness and a thinner damaged layer. Therefore, control of the size of SiO_2 abrasive particles and the uniformity of the particle size distribution are important parameters in ensuring the uniformity of surfaces in the CMP process.

4. Conclusions

This study focuses on the effects of SiO_2 abrasives on polishing performance during CMP of a steel substrate. All in all, the polishing steel substrate was measured by CMP SiO_2 slurries. Their roughness reduced from 128 to 8.4 nm while the size of nanoparticles decreases from 684 to 58 nm. The material removal amount reduced from 334 to 113 nm as the size of nanoparticles decreases from 684 to 58 nm.

SiO_2 nanoparticles were prepared with the use of sol-gel method as CMP slurries. It could produce higher chemical purity and ultrafine particles with a narrow size distribution. SEM results reveal that CMP with these SiO_2 slurries yielded surfaces of high quality. Finally, the CMP mechanism of the steel substrate was determined.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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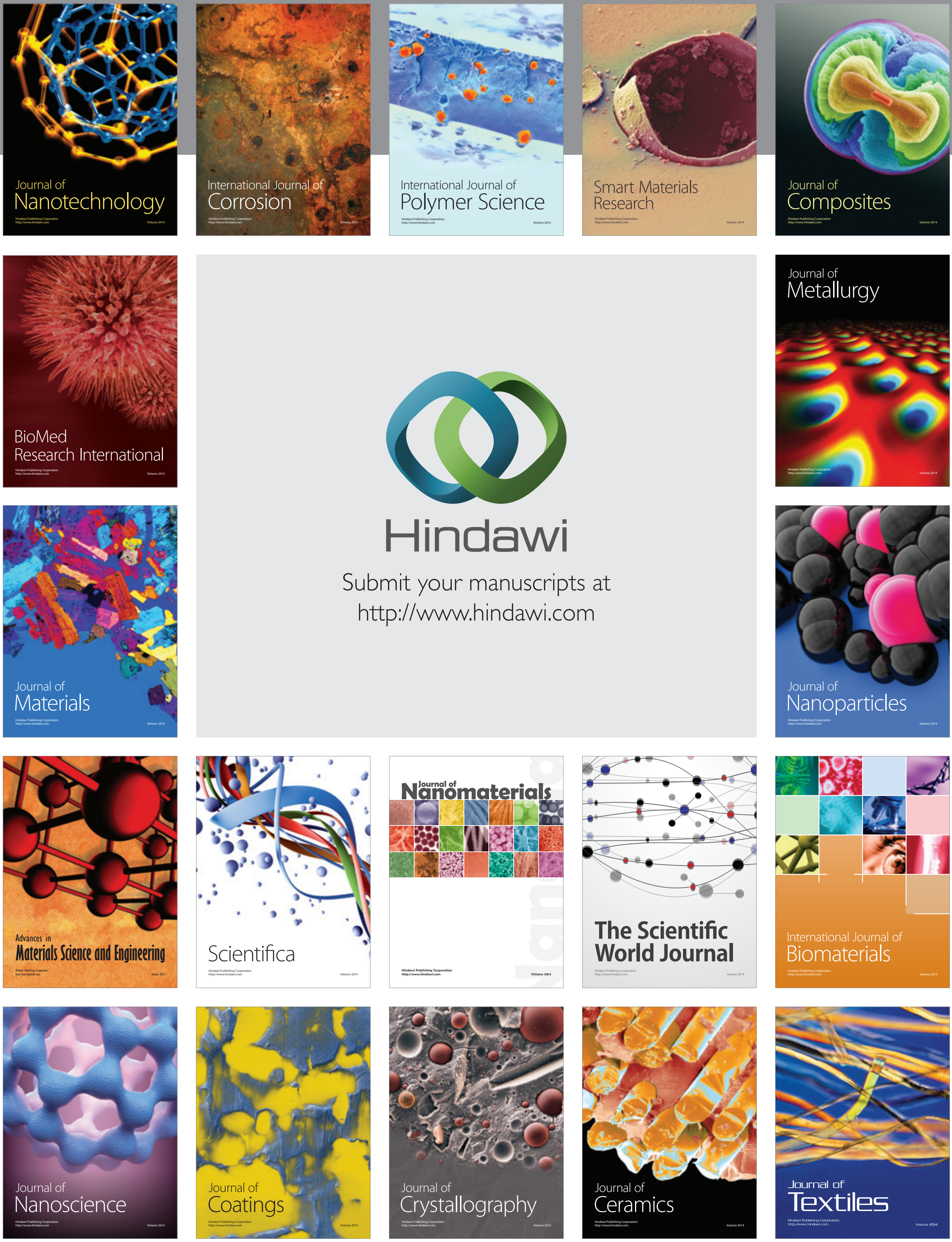
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