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CHEMICAL MECHANICAL POLISHING BY COLLOIDAL SILICA SLURRY

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ABSTRACT

Chemical Mechanical Polishing is a unique process enabling technology that allows chip makers to readily drive lithographic patterning steps to smaller dimensions, an ages old, "retro" technology related to glass polishing and metallographic finishing, thus enabling optical lithography to work. It represents a situation that is a true paradigm shift from the typical way in which technological advancements become main stream in high-technology semiconductor manufacturing processes. Colloidal nano-abrasives with different particle sizes are required for slurries in different CMP processes. Colloidal silica is used as polishing slurry for producing reflecting surfaces for mirrors, lenses and the planarization of computer chips. Industrial use of colloidal silica's is growing steadily in both traditional areas and ever-increasing numbers of novel areas. Colloidal silica's are found in fields as diverse as catalysis, metallurgy, electronics, glass, ceramics, paper and pulp technology, optics, elastomers, food, health care and industrial chromatography, polishing sophisticated microcircuit parts to outer space and play vital role in the safe reentry of space vehicles and the development of Western for that matter, world civilization. The paper focuses a brief overview of chemical mechanical polishing using colloidal slurry.

Keywords - Chemical Mechanical Polishing, Colloidal silica, Nanoabrasives, Slurry, Semiconductor

I. INTRODUCTION

Chemical mechanical polishing (CMP) technology was first put forward by Monsanto [1-3] in 1965. It is an indispensable process step in semiconductor device fabrication, common technique used in wafer polishing for dynamic memory, microprocessor applications and glass mechanical polishing. It is one of the key new nanotechnology fabrication processes, a true advance that could be made to work despite enormous odds and technical difficulties early on. Chemical mechanical polishing (CMP) is widely used in the semiconductor industry [4-7] to produce mirror like surfaces with no measurable subsurface damage. The application of scientific technological results in the domain of glass polishing with suspensions of rare earth oxides and micro heterogeneous suspensions with particle dimensions of 0.1–0.5 μm diameter and new or tested abrasive ultra disperse powders (UDP) have been attempted in electronics. The Chemical mechanical polishing performances can be optimized by process parameters such as equipment and consumables (pad, backing film, and slurry). One of the critical consumables in the CMP process is slurry (typically containing both abrasives and chemicals acting together), that directly affects CMP efficiency and the yield. Slight changes in slurry properties due to contamination, chemical degradation, abrasive content or applied shear can change polish performance and impact yield. Correlation of slurry property measurements with evaluations of wafer polish rate, planarity and defectivity provides insight into the root cause of degradation in polishing. The conventional slurry consists of abrasive particles of the solid state suspended in a liquid state chemical solution **[**8**]** containing one or more of various chemicals such as oxidizers, pH stabilizers, metal ion complexants and corrosion inhibitors [9]**.** An abrasive in the slurry provides both mechanical action with nanometer-sized abrasive particles and chemical action from the solution additives with a synergistic effect that causes material removal [10,11].Through chemical and physical actions, the abrasive-liquid interactions play an important role in determining the optimum abrasives' type, size, shape and concentration [12]. The slurry designed for optimal performance should produce reasonable removal rates, acceptable polishing selectivity with respect to the underlying layer, low surface defects after polishing and good slurry stability. Choosing slurry which provides good removal rates without causing defects is of utmost importance in CMP. Colloidal sized SiO_2, CeO_2 and Al_2O_3 particles are used in the manufacturing of CMP slurries. They are applied in different fields, but SiO_2 is promising. Alumina particles find limited used in the manufacturing of slurries for tungsten CMP; they are slowly falling out of vogue because of their hardness[13], Today, silica particles are predominantly used in the preparation of slurries for dielectric as well as metal CMP. The use of industrial sols–gels of silicon acid (Monsanto

Comp, Dupoint, Nalco Ch et al.) and of compositions based on aerosol type UDP SiO_2 (Siemens,Degussa) and Al_2O_3 (Union Carbide Corp.) led to the development of colloidal silica. Robert Walsh (Monsanto), patent and publications of other authors (H. Dersin, I.S. Basi, R.L. Lachapelle, et al.) up to the beginning of eighties contributed to development in microelectronics with the development of colloidal silica sol and silica gel. In this paper a brief review of CMP process using colloidal silica slurry is presented.

II. COLLOIDAL SILICA SLURRY

The silica slurries are typical consumable materials for CMP. The colloidal silica and fumed silica are known as the representative CMP slurry materials. Colloidal silica polishing suspensions are unique because they provide both dispersing action as well as a chemical mechanical polishing (CMP) action. It is effective as an additive for the intermediate diamond polishing of metals and is also the best polishing abrasive for eliminating subsurface and surface because of its CMP polishing action. These polishes are chemically stabilized to produce a nearly “perfect suspension”; can also have additives that minimize the effect of particle aggregation of crystallization. The distribution of colloidal silica has an important effect on polishing rate and polished surface roughness.

In 2001, the effects of temperature, slurry pH, applied pressure and polishing rotation rate on the material removal rate during chemical mechanical polishing (CMP) of 4H-silicon carbide wafers using colloidal silica slurry and polyurethane/polyester fiber polishing pads have been studied by Neslen C.L et al [14]. The wafers were polished for 30 or 60 mins using a Strasbaugh Precision Polishmaster with a random motion polishing armature. Polishing at wafer temperatures of 23^0C and 65^0C were performed and found that increased temperatures had no significant improvements in removal rate. The polishing slurry pH levels for the 90 rpm study were similar to 60 rpm, showed that material removal rate was not affected by pH. Increased applied pressure resulted in accelerated removal of wafer material. The average removal rate over the four-hour period using a 9.9 pH polishing slurry was 139 Å/hour while an pH 11 polishing slurry was only 108 Å/hour., the variability in the removal rate during 150 rpm was high and ranged from 298 Å/hour during the second 30 min polish to 1860 Å/hour during the last 30 min polishing interval due to the inability to maintain a constant amount of polishing solution on the pad during the polishing interval. Excessive pressure resulted in damage of polishing pad and increased wafer preparation costs. Polishing pad rotational speeds had the greatest impact on wafer material removal rates with an associated increase in removal rate variability. The authors concluded that additional rotational speed studies would be useful to maximize material removal rate with decreased variability

The effects of phosphoric acid addition on slurry for chemical–mechanical planarization (CMP) of copper and tantalum nitride were investigated by [15]. Alumina or colloidal silica as an abrasive, organic acid as a complexing agent, Hydrogen peroxide (H_2O_2) an oxidizing agent, a film forming agent, a pH control agent and additives, phosphoric acid (H_3PO_4) as accelerator of the tantalum nitride as well as hydrogen peroxide as stabilizer were used. Experiments were performed on G&P Technology POLI-500CEk chemical–mechanical polisher ,Rodel IC-1400 k-groove polyurethane pad with the head speed and the table speed 40 rpm, down pressure of the head 7 psi , slurry flow rate 150 ml/min, polishing for 1 min on electroplated copper, sputtered tantalum nitride, PETEOS wafer with 10,000 A° thickness. Zeta potential and particle size measurement of the slurries were carried out by using the Brookhaven ZetaPlus instrument. An acceleration of the tantalum nitride CMP was verified by electrochemical curves recorded with an EG and G 273A potentiostat. The slurry of 5.0% by wt. abrasive, 5.0% by wt hydrogen peroxide, 0.5% by wt. phosphoric acid had good H_2O_2 stability and TaN acceleration and dispersion ability. Hence slurry including phosphoric acid was proposed.

Hong Lei prepared novel colloidal SiO_2 slurry, a carboxylic acid containing a long alkyl chain as lubricant additive, for the chemical–mechanical polishing of disk substrates with NiP plated [16]. Polishing tests were conducted with SPEEDFAM-16B-4M CMP equipment (SPEEDFAMCo. Ltd., Japan) for four slurries, each with a different mean particle diameter of 15, 30, 50 and 160 nm, processing pressure of 70 g/cm^2, rotating speed of 25 rpm, processing duration of 8.5 min and slurry supplying rate of 300 ml/min on work pieces of 95 mm/1.25mm aluminum alloy substrates with NiP plated about 85 wt. % nickel and 15 wt. % phosphorus element. Prepared slurry of 6 wt. % SiO_2 particles with an average diameter of 30 nm, 1 wt. % ferric oxidizer and 2 wt. % lubricants in DI water at pH value of 1.8, exhibited smoother polished surface. The abrasive particle size, contents of oxidizer, lubricant additive and abrasive particle contained in the prepared colloidal SiO_2 slurry as well as pH value of the slurry, had strong impact on the average roughness (Ra), the average waviness (Wa) and material removal rate. Better surface quality resulted, with smaller SiO_2 size, moderate SiO_2 concentration, lower oxidizer content, higher lubricant content and moderate pH value under the testing conditions, while the high material removal rate with large size SiO_2 , high particle, oxidizer contents and low lubricant content.

The chemical mechanical polishing (CMP) of aluminum and photo resist using colloidal silica-based abrasive (average ~20 nm diameter,Ace Hitech) ,effects of varying slurry pH, silica concentration and oxidizer concentration on surface roughness(Rv) and removal rate were investigated by [17] in order to determine the optimum conditions for these parameters. Experimentation was conducted on a modified Motopol 2000 polishing system from Buehler Co. with Polytex Supreme pad from Rodel. H_3PO_4 and KOH were added to adjust the pH of colloidal silica with de-ionized water. In the Al CMP, H_2O_2 was used as an oxidizer. In all experiments, the polishing pressure was 30 kPa, the linear polishing velocity was 15 m/min and the slurry flow rate of 12 ml/min with polishing times of 4 and 1 min for Al and PR respectively. The measurement was carried out under a sampling length of 10 mm, a cut off length of 0.08 mm and a scanning speed of 25m/s by Dektak (Veeco Instruments).The removal rate of Al was measured by a four-point probe (Chang Min Tech) and PR removal rate was measured under a wave length of 480 nm and a reflective index of 1.63 by a NanoSpec (Nanometrics). The Rv values of the Al and PR surfaces before the CMP were 39.4 and 7.85 nm, respectively. The results of the CMP of the aluminum with the colloidal silica-based slurry were good with small micro-scratch size when Rv ≤ 10 nm and large removal rate for the slurry pH of 2–4 and the oxidizer H_2O_2 concentration 1–3% by vol. The colloidal-based silica slurry produced a desirable fine Al surface with few micro-scratches similar to filtered alumina-based slurry, but produced a photo resist surface with many micro-scratches as shown in table.1. The Fig1a, 1b and Fig 2a, 2b represent roughness and removal rate of Al and PR as function of slurry pH and SiO_2 concentration.

Table: 1

Thinfilm	Abrasive	Rv (nm)	RR (nm/min)
Al	Al_2O_3	18.15	21.34
Al	Filtered Al_2O_3	9.85	2.57
Al	Colloidal SiO_2	6.08	137.45
PR	Al_2O_3	13.31	1874.95
PR	Filtered Al_2O_3	5.96	248.01
PR	Colloidal SiO_2	15.27	203.01

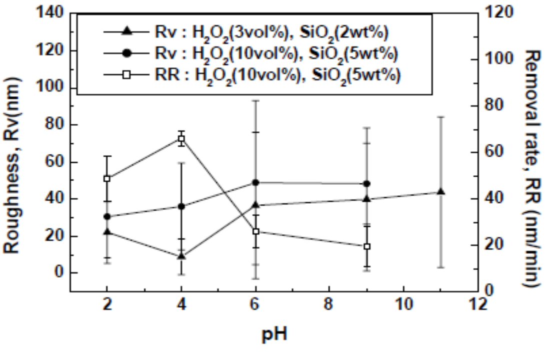

Fig 1.a

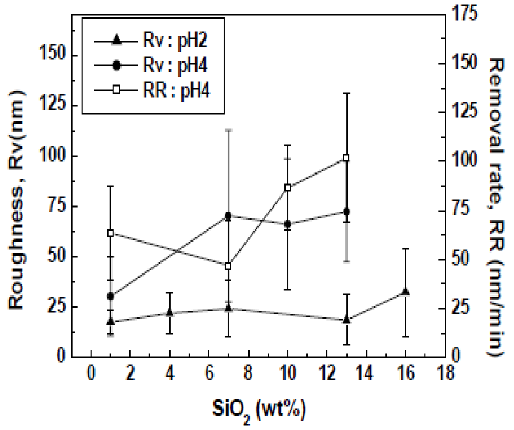

Fig 1.b

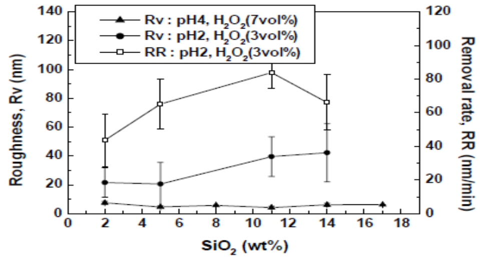

Fig.2 a

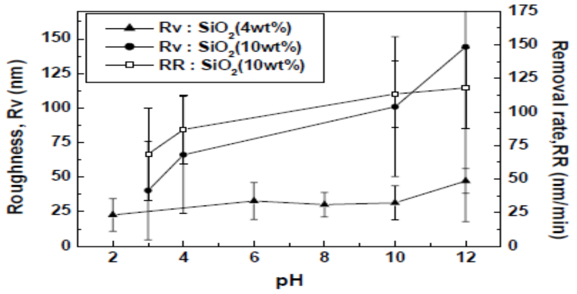

Fig. 2b

New semi-abrasive free slurry for copper chemical mechanical planarization (CMP) was investigated through the addition of acid colloidal silica below 0.5% by wt, hydrogen peroxide and other additives by [18]. The additives as stabilizers for hydrogen peroxide as well as accelerators in tantalum nitride CMP were also evaluated. Experimentation was carried on G&P Technology POLI-500CETM chemical mechanical polisher using Rodel IC-1400 k-groove polyurethane pad. Electroplated copper wafer with 1600 nm, sputtered tantalum nitride wafer, PETEOS wafer with 1000 nm thickness were used for polishing. SKW 6-3 copper wafer was used as a patterned wafer with 0.25 μm minimum feature size. For the polishing, down pressure of the head 4.3 psi, slurry flow rate 300 ml/min, head speed and table speed was set at 50 rpm. The Zeta potential and particle size measurement of the slurries were carried out using Brookhaven ZetaPlus instrument. Electrochemical curves were recorded with EG&G 273A Potentiostat. Metal impurities measurement of the slurry was carried out by PerkinElmer ICP-Mass instrument. Zeta potential change of colloidal silica in slurries with and without the addition of additives as a function of pH is shown in Fig. 3. When surfactant was added to colloidal silica slurry, zeta potential increased from 0 and a sudden reversal of charges was observed in pH 2–3 range. Particle dispersion with the chemical-added colloidal silica slurry in pH 2.5 was stable during 90 days. A copper wafer dipped in chemical added colloidal silica slurry was clearer than a wafer dipped in the slurry without the chemicals. Good hydrogen peroxide stability, excellent colloidal silica dispersion ability and easiness of post-CMP cleaning were provided by the semi-abrasive free slurry. The extent of enhancement in tantalum nitride CMP was verified through an electrochemical test. Ammonium and amine became very stable, indicating that decomposition rate was below 0.001 wt%/day. So this type of slurry was formulated in a single package rather than conventional, uncomfortable two-package system due to unstable hydrogen peroxide.

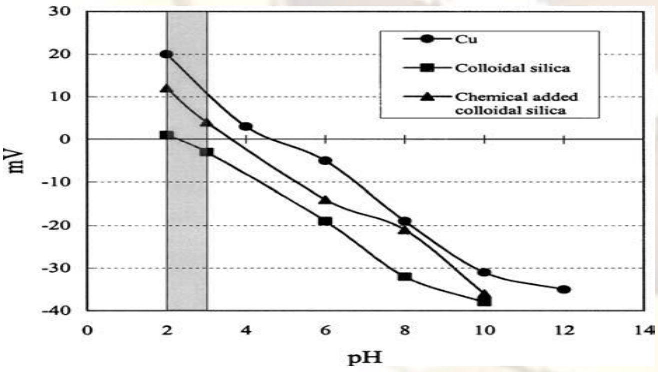

Figure 3 Zeta potentials of copper, colloidal silica and chemical added colloidal silica

Shao-Yu Chiu et al. [19] investigated the removal mechanism of Cu-CMP on the characteristics of colloidal-silica-based slurry. All polishing experiments were performed with (100) oriented, 6-inch-diameter p-type Si wafers. The polishing sample was stacked with 900-nm-thick, 50-nm-thick Cu and Ta respectively. Multi-step chemical mechanical polishing (CMP) with different copper removal rates and polishing pads was used to eliminate topography efficiently and to reduce micro-scratches on copper films. Cu-CMP was performed with a Westech Model 372M polisher using a Politex Regular E. pad. Polishing parameters such as down force, platen/carrier rotary speed, back pressure and slurry flow rate were set to be 5 psi, 42/45 rpm, 2 psi and 150 ml/min respectively. Polishing slurries with diluted colloidal silica (<50 nm in size) 10% by wt, 10 wt. %H_2O_2 (30 wt. % semiconductor grade), Potassium hydroxide (KOH), ammonium hydroxide (NH_4OH) and tetra-methylammonium hydroxide (TMAH) were used as slurry pH adjusters. A laser diffraction particle size analyzer, UP-150 was used to measure the aggregation size of abrasives in slurries. In colloidal-silica-based slurry, the polishing behaviors of copper, tantalum and silicon dioxide were found to relate to alkaline additives. The size of cations from alkaline additives influenced the zeta potential of slurries, so as to vary the material removal rate. It was found that the polishing behavior of Cu, Ta and oxide was deeply dependant on the slurry pH and the surface charge-related interactions between the slurry and the polishing substrate. The maximum removal rate of Cu was above130 nm/min at pH2. As slurry pH increased into neutral regime, the removal rate of Cu dropped by formation of Cu oxide passivation (Cu_2O, CuO). The attraction and expulsive force affected the impacting frequency between colloidal silica abrasives and the wafer surface. The iso-electric potential of colloidal-based slurries was around pH2 which led to higher Ta removal rate. NH_3 dissolved Cu oxide passivation and formed Cu $(NH_3)_4^{2+}$ to enhance the removal rate of copper. The removal rate was about 225nm/min for Cu and 80nm/min for Ta at pH9.2. With more NH_4OH added into the slurry at pH10, the removal rate was enhanced to 1490 nm/min for Cu and 100nm/min for Ta. Large-size cations led to less impacting frequency between the abrasives and the substrate, to get lower removal rate. KOH was found to be a suitable pH adjuster for the colloidal-silica-based slurry. High or low removal selectivity of Ta/Cu and SiO_2/Cu during the two-step Cu-CMP process could be achieved by modified colloidal-silica-based slurries with proper alkaline additives and pH values.

The effects of varying the size and the concentration of the abrasive in colloidal silica slurry and the concentration of tetra-methyl ammonium hydroxide (TMAH) were investigated in terms of the oxide film loss, the removal rate, the roughness of the film surface and polysilicon-to-oxide film removal selectivity. These effects were investigated [20] performing chemical mechanical polishing (CMP) experiments under polishing pressure 13.8 to 41.4kPa, relative velocity between the pad and the wafer 0.539 m/s and the polishing time 30 s on conventional 8” silicon wafers prepared by using the single side polishing method. Nanoscale colloidal silica slurries (PL-3 and PL-7, Fuso Chemical Inc., Japan) containing two different spherical abrasive particles with primary sizes of 30 and 70 nm were used in these experiments. The colloidal silica slurry was dispersed in deionized water and stabilized by adding 0.06 wt% of a commercially available nonionic organic polymer (poly(acrylamide), PAAM) along with quaternary ammonium hydroxide compound (TMAH) up to 0.52 wt% , wet etchants for polysilicon, a cellulosic polymer (hydroxyethyl cellulose, HEC), molecular weight of 50,000, at a constant concentration of 0.001wt% was optionally added. The morphology of the colloidal silica abrasives was observed with a high-resolution transmission electron microscope (HRTEM; JEM-2010, JEOL, Japan). The secondary particle size was measured by using acoustic attenuation spectroscopy (APS-100, Matec Applied Sci., U S A.). The surfactant pH was measured with an advanced benchtop pH meter (Orion-525A, Thermo Orion, U.S.A.). The rheological behavior of the slurry suspensions examined with a controlled-stress viscometer (MCR300, Paar Physica, Germany). Average size, pH and conductivity increased with the TMAH concentration. The removal rate of the polysilicon film reduced with high pH value in the range of 10 to 12 due to change in the polysilicon surface from hydrophobic to hydrophilic. The abrasive behavior in the slurry was less affected by abrasive size and TMAH concentration. Higher polysilicon to oxide removal selectivity was directly related to the zetapotential curves of the oxide , polysilicon films and the modified abrasive particles in the colloidal silica slurry. It was found that with increasing TMAH concentration, the removal rate and the polysilicon-to-oxide selectivity were reduced after an initial increase, regardless of the abrasive size in the slurry. Within a TMAH concentration range of 0.06 to 0.52 wt%, the removal selectivity at a lower abrasive concentration for abrasive size of 30 nm was slightly higher than for higher abrasive concentration in case of a smaller abrasive, but in the case of a larger abrasive the removal selectivity was almost independent of the abrasive concentrations. The oxide removal rate was maintained at 40 to 60 °A/min during the polishing process. At a lower TMAH concentration the surface roughness, became worse. The results qualitatively suggested a mechanism in which OH^- ions bonded to the Si surfaces of the abrasives in the slurry and attached to the surface of the polysilicon film.

In paper [21], the polishing mechanism of LN , discussed based on the results of an integrated analysis considering mechanical, chemical and thermal factors. Research and development CMP equipment, POLI-400 (G&P Technology Co.), was used in the experiments. The slurry was formulated by adding colloidal silica abrasive (average ~120 nm diameter, pH 10.7, Ace Hitech Co.) and a foamed crosslinked polymer pad, IC 1400 k-groove (Rohm & Hass Corp.), was used. The Material Removal Rate (MRR) was investigated by XPS and nano-indenter analysis. The MRR increased with low pH slurry in both cases with H_3PO_4 and HNO_3. HNO_3 had a stronger effect on the MRR than H_3PO_4. High quality surfaces (Ra < 2 nm) were obtained with pH 3 and 7. The higher abrasive concentration and low pH slurry induced high MRR. The flow rate was controlled from 50 cc/minute to 500 cc/minute (50, 100, 300, 500 cc/minute) in the experiments. As the flow rate decreased, the material removal rate increased due to frictional heat, the thermal energy and chemical activation energy. The reaction layer formed on the LN surface showed a variation of hardness with NbO_2, Nb_2O_5 and changed MRR.

The optimum condition selection of ultra precision wafer polishing and the effect of polishing parameters on the surface roughness, temperature variation were evaluated by Eun-Sang Lee et al.[22] using central composite designs such as the Box-Behnken method, one of response surface analyses. The polishing process was performed over the whole wafer surface when the polishing pad rotational velocity and wafer rotational velocity was same. silicon wafer 4-inch, environmental temperature 21.5℃, humidity 43%, Polyurethane based Suba 600 made by Rodel Inc. as polishing pad and commercial colloidal silica based slurry with particle size in the 50- 70 nm range were used. Pressure, wheel speed and process time which were used as factors in this experiment affected surface roughness of wafer under the final polishing processes. A second-order regression equation for the surface roughness was developed from the experimental data. The regression equation induced by response surface model was evaluated to select proper polishing conditions with constraints of the surface roughness. The effect of changing final polishing parameters on the surface roughness has been investigated and the ideal optimum condition has been researched. At each ranges of pressure, with increase in wheel speed and process time, surface roughness decreased initially and then increased. Optimum condition for surface roughness was 0.2MPa of pressure, 30 rpm of wheel speed and 10 minutes of process time. The frictional heat between polishing pad and wafer during the final wafer polishing increased with range increment of each process parameters. As the temperature increased, there was increase of the effect by a chemical reaction and a variation of pH so that the removal rate of wafer increased in proportion to the temperature. The temperature elevation affected the increase of the removal rate.

Chemical mechanical polishing (CMP) of commercially pure Titanium (Ti) was carried out using two types of slurries, acidic (pH of 3.2 adjusted by H_3PO_4 and $NH_4H_2PO_4$) and basic(pH of 9.8) colloidal silica (MasterMet 2, Buehler, IL, USA) with a mean grain size of 0.06μm containing H_2O_2 up to 3% by wt termed as 3BCS and 3ACS respectively. Experiments were performed on the automatic polisher for 15 minutes under a polishing pressure of 1 kg/cm^2, slurry dropped on a buffing cloth (Chemomet I, Buehler, IL, USA). The specimens Titanium ingots, 16 mm in diameter (equivalent to JIS Class 2; T-Alloy M, GC Corp., Tokyo, Japan) were ultrasonically cleaned in acetone for 5 minutes after CMP and then dried by blowing air. Polishing behavior and surface properties were investigated by [23] using a commercial atomic force microscope (AFM) (JSPM- 4210, JEOL, Tokyo, Japan), EPMA (EPMA-8705-HII, Shimadzu,Kyoto, Japan), X-ray photoelectron spectroscopy (XPS) (Quantum 2000, ULVAC-PHI Inc., Chigasaki, Japan). Multiple analysis of variance showed the effects H_2O_2 concentration and slurry pH on weight loss were highly significant ($p<0.01$). Surface roughness gradually decreased with increased concentration of H_2O_2, independent of slurry pH. Weight loss of Ti polished using the basic slurry was larger than that using the acidic one and surface roughness was less than 2 nm with basic slurry of 3 wt% H_2O_2. The thicknesses of their oxide films were estimated to be 6.7 nm and 7.7 nm respectively. H_2O_2 concentration, up to 6%by vol, resulted in higher Ti oxidation rate and increased removal rate. Higher pH values (2 to 6) resulted in increased Ti removal rate. Chemical species of three kinds, OH^-, O_2^- and H_2O were detected on the Ti surfaces with peak binding energy values of 530.3, 532.0 and 533.2 eV respectively. Fig 4 shows the Elemental analysis of the polished surfaces by EPMA. Results of this study showed that CMP using colloidal silica containing H_2O_2 successfully created a mirror-polished surface without contaminated and reacted layers.

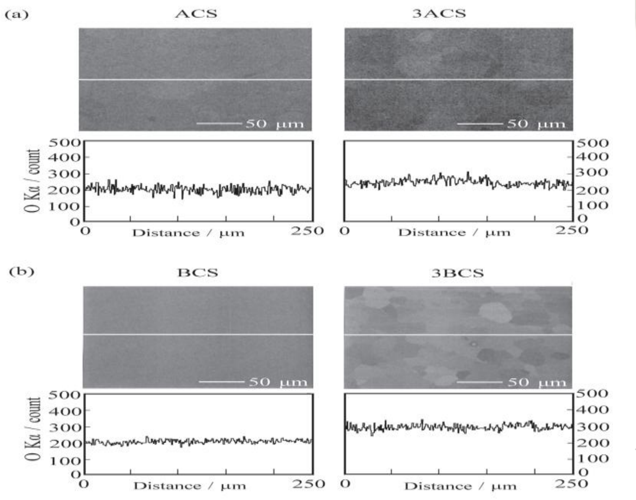

Fig. 4 SE images of the surfaces polished with CMP and O Kα line profiles. The location of an O Kα profiling was indicated by a line on the corresponding SE image. (a) Treated with colloidal silica slurry of pH 3.2 (ACS) and ACS containing 3 wt%H_2O_2 (3ACS). (b) Treated with colloidal silica slurry of pH 9.8 (BCS) and BCS containing 3 wt% H_2O_2 (3BCS).

The material removal rate (MRR) was investigated by [24] to learn how long the CMP process continues to remove a damaged layer by mechanical polishing using 100 nm diamond and the dependency of mechanical factors such as pressure, velocity and abrasive concentration using a single abrasive slurry(SAS) and focused on the epi-ready surface with a mixed abrasive slurry (MAS). A 6H-SiC wafer, crystallized by physical vapor transport (PVT), colloidal silica slurry, POLI-400 (G&P Technology CO.) was used during the experiments. With the increased pressure, velocity and concentration of an abrasive the MRR also increased. SAS (only colloidal silica and nanodiamond abrasive) and MAS (colloidal silica + nanodiamond) were used for the SiC CMP. The surface roughness was improved with MAS up to 2.4 Å as analyzed from AFM images. The scratches were not completely removed and the MRR decreased with increase in the abrasive concentration (0.25 mg/h).The addition of nanometre sized diamond in the MAS provided a strong synergy between mechanical and chemical effects. Through the experiments, chemical effect (KOH based) was essential and the atomic-bit mechanical removal was found to be efficient to remove residual scratches. With increased concentration of nano-diamond, surface roughness and the condition of scratches were improved, MRR was increased up to 0.6mg/h. SiC CMP mechanism was quite different from that of relatively softer materials to gain both high quality surfaces and a high MRR. The reaction of wafer surfaces by X-ray Photoelectron Spectroscopy (XPS spectra) of SiC substrate submerged into the KOH based slurry for 24 hours is shown in fig 5

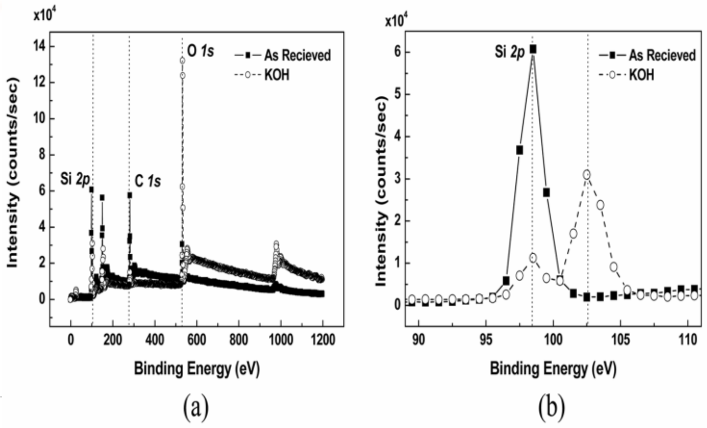

Fig.5 XPS spectra of : (a) Survey and (b) Si 2p from SiC surface of as-received and dipped in KOH based slurry.

Xiaokai Hu et al [25] studied monodisperse colloidal silica nanoparticles ranging from 60 to 130 nm in diameter as abrasives in chemical mechanical planarization/polishing (CMP) process of integrated circuit (IC) manufacturing. The physicochemical properties of the silica synthesized were characterized by the X-ray diffraction (XRD) patterns and thermal analysis. Three inch polished silicon wafers (P type and (1 1 1) orientation) were subjected to CMP testing on a CETR CP-4 machine (CETR, Inc., Campbell, CA) using the slurry consisting of colloidal silica with pad made of IC1000 type with grooves, from Rohm & Haas Co. The material removal rate (MRR) was determined on the basis of weight loss before and after polishing and the surface quality were evaluated by means of the atomic force microscopy (Q-ScopeTM250 AFM) and scanning electron microscopy. The silica nanoparticles, amorphous in structure as compared to crystalline quartz, possessed a relative density of 93%. The as-grown large sized silica nano particles applied as abrasives in CMP slurry to polish silicon wafer, achieved MRR of 430 nm/min and RMS roughness of less than 0.97 nm.

The effect of particle size from 40 to 120 nm and surfactant from nonionic to anionic and cationic on MRR and surface roughness by chemical mechanical polishing (CMP) of glass using colloidal silica-based slurry was explored by Zefang Zhang et al. [26]. Four colloidal silica-based slurries with different particle sizes from 40 to 120 nm and three typical surfactants from nonionic to anionic and cationic were used to investigate their effects on glass CMP. The surfactants were selected from cationic surfactant cetyl tri methyl ammonium bromide (CTAB), anionic surfactant OROTAN 1124 [poly-(acrylic acid) sodium] and nonionic surfactant AEO∼ 9 (Peregal). Two inch glass substrates of chemical composition of SiO_2 (70–73%), Na_2O and K_2O (13–15%), CaO (7–12%) were polished using a CMP tester (CETR CP4) with an IC1010 grooved pad (Dow Electronics). The pad was conditioned prior to each polishing for 5 min using a 4 inch diamond grit conditioner. The polishing process parameters at room temperature were set as follows: pad and wafer rotation speed rotation speed 100 rpm, relative velocity 134 cm/s, down force 5 psi, feed rate of the slurry 120 ml/ min and polishing time 10 min. The surface roughness was measured from an area of 10μm×10 μm using AFM and found surface finish of glass surfaces was independent of the particle size. The material removal rate strongly depended on the particle size and the types of surfactants. The root mean square roughness was independent of particle size and correlated to surfactants. MRR increased with 0particle size from 40 to 60 nm but decreased with particle size changing from 60 to 120 nm. On the basis of polishing results, it was concluded that the main polishing mechanism was changed from indentation mechanism to surface-area mechanism at the critical point of 60 nm, with the variation of particle size. In the surfactant test, nonionic surfactant AEO ∼ 9 showed the highest MRR, while anionic OROTAN 1124 gave the best surface quality. Cationic Cetyl tri methyl ammonium bromide (CTAB) showed the lowest MRR and worst surface quality. The molecular structure, charge type and lubricating effect of the surfactants played an important role in the dispersion of abrasive particles and in the CMP performance.

Chemical mechanical polishing (CMP) experiments were performed to study the effects of polish pressure, pad rotational speed, polish head rotational speed and slurry supply velocity on the flatness, surface finish of the polished optical silicon substrates and on the material removal rate (MRR) [27]. Single-crystal (100) silicon substrates with a thickness of 6 mm and a diameter of 76.2 mm(3 in.) were polished on an Okamoto SPP-600S CMP machine, a conditioning head, a polishing head and a ϕ600-mm polishing platen with fabric cloth pad (3M 300LSE) on it. Commercial colloidal silica slurry (NYACOL®9950) was diluted with DI water and stirred by a magnetic stirrer during the polishing experiments. Both the specially designed carrier and the substrate were mounted onto a backside film of the polishing head prior to each test holding under vacuum pressure of -90 KPa. Oscillation motions of the polishing head and conditioning head relative to the pad were applied with an oscillation speed of two strokes per minute and an oscillation width of 10 mm. The optimal process parameter setting obtained from the design of experiments were average MRR for the optical silicon substrates polished at a polish pressure of 9,800 Pa was 88% higher than that at 4,900 Pa and at a pad rotational speed of 20 rpm was 171% higher than that at 40 rpm due to the distribution of colloidal silica slurry in the perimeter area of the polishing pad. The combination of a polish head rotational speed of 20 rpm and a slurry supply velocity of 100 ml/min resulted in the lowest average flatness value. The goal to attain optical silicon substrates with nanometric surface roughness and micrometric flatness by an optimized CMP process with a high MRR with reduced polishing time to only 15 min from over 8 h has been achieved.

III. CONCLUSIONS

The silica based compositions are applied successfully for the finish polishing of Si, Ge, GaAs, InP, variety of materials, metals, dielectrics and other semiconductors in industries. Experimental, theoretical ideas were considered to develop new efficient colloidal compositions. Investigations into the kinetics and mechanisms of the processes proceeding by the CMP and the development of polishing compositions and technology (including equipment upgrading) will progress further. The persistence of the CMP in semiconductor technology, its competitiveness and its compatibility with other nanotechnologies over a long time, infer new scientific and technological breakthroughs. Further research regarding the influence of the diverse mixed conditions will be continued. Imagination is the only limit to the range of uses that scientists will find for old and new forms of colloidal silica to contribute to CMP and the quality of life of people around the world.

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