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Effect of Chemicals and Slurry Particles on Chemical Mechamical Polishing of Polyimide

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The purpose of this study was to investigate the effect of chemicals and particles on chemical mechanical polishing (CMP) of polyimide (PI). The effect of particle size and its surface area on both the removal rates and the surface roughness was investigated as a function of the slurry content upon the addition of various chemicals. The optimal particle content was measured for silica, ceria and alumina slurries in terms of the removal rate and surface roughness. The removal rate was highest when deionized (DI)-water-based alumina slurry was used. However, the greatest surface roughness was measured when ceria slurry was used rather than alumina. Alkaline chemicals were added to the slurry to enhance the removal rates of PI during CMP. The addition of Tetramethyl Ammonium Hydroxide (TMAH) and Potassium Hydroxide (KOH) to ceria slurry but not to alumina and silica slurries increased the removal rate significantly at higher pH values. The addition of ethylenediamine and the presoaking of PI in hot DI water did not increase the removal rate in alkaline-chemical-based slurries. The addition of surfactant resulted in a decrease of the removal rate to half of that determined without the addition of surfactant.

KEYWORDS: CMP, polymide, low *k* materials, slurry, removal rate, surface roughness, alumina particles, silica particles, ceria particles

1. Introduction

As device feature size is reduced to the deep submicron level, minimizing power dissipation, crosstalk noise and propagation delay due to resistance-capacitance (RC) coupling become significant due to increased wiring capacitance, in particular, interline capacitance between metal lines on the same metal level. The combination of a low-resistivity metal and low-dielectric-constant (low-*k*) interlevel dielectric (ILD) should yield a high-performance interconnection.[1,2] IBM recently introduced the Cu damascene process[3] and many low-*k* materials have been investigated using the Cu chemical mechanical polishing (CMP) process. Organic polymers are attractive for application to ULSI device fabrication due to their low-*k* characteristics, high breakdown field strength, low bulk leakage and low stress.[4] However, these organic polymers exhibit a glass transition temperature lower than 400°C.[5] It is one of the challenges in this field to find an organic polymer stable above 450°C. Polyimide (PI) among organic polymers meets the temperature requirements and has good mechanical and electrical properties.[6] Polyamic acids are synthesized by the condensation reaction of a dianhydride and a diamine. A polyimide is then formed by the heating of a polyamic acid precursor that removes water by a cyclization reaction.[6,7]

Among the many planerization techniques available, CMP has become the most important in the fabrication of devices with multilevel metal interconnections because of the increased film thicknesses and more stringent requirements in the photolithograpy process.[8] In addition, CMP is a key procedure in the Cu damascene process.

Because polymers, unlike metals, do not form a passivation layer during CMP, the CMP mechanism in polymers may be different from that in metal CMP. In addition, they are inherently soft materials, and are more likely to develop scratches and show different types of mechanical damage from those observed on oxides and metals during CMP. Scratches in polymer ILDs are likely to cause considerable current leakage and lower the breakdown strength. The mechanical components in the polishing must be carefully controlled along with the chemical components to obtain a reasonable removal rate without producing scratches on the surface during polymer CMP.[9]

In this study, CMP of PI as a low-*k* material was investigated. The effect of slurry particles on the removal rates and surface roughness was studied to understand the mechanical aspects of PI CMP. In addition, various chemicals as PI etchants were evaluated. The slurry content and concentrations of chemicals were varied during CMP to optimize the removal rates and surface roughness.

2. Experimental Procedures

For the experiments, bare silicon and thermal-oxide (600 nm)-coated silicon wafers were used as the substrates. They were precleaned in a mixture of H_2SO_4 and H_2O_2 (4 : 1), followed by HF treatment, and finally rinsed with high-purity deionized (DI) water (18.2 MΩcm, manufactured by Millipore Milli-Q Plus). PI (PI2611) and an adhesion promoter (VM651) were purchased from HD MicroSystems. Figure 1 shows the chemical structure of the PI used in the experiment. The PI film was spin-coated in two steps by a spin-coating system (Laurell Technologies) at 800 rpm and 6000 rpm for 30 s each. The spin-coated wafer was precured in a convection oven at 150°C for 30 min and then cut into 1.5 cm × 1.5 cm segments using a sawing system. The cut specimens were cured in an Infrared Gold Image Furnace from Ulvac Sinku-Riko Inc. at 350°C for 1 h in an N_2 atmosphere. The final thickness of the polyimide film was between 2.3 and 2.7 μm. Also, a nonionic surfactant, Triton X-100, was used without further purification for the experiment.

γ-alumina of 0.05 μm diameter was purchased from Buehler Co. Fumed silica of 0.014 μm diameter was obtained from Sigma Co. Ceria particles were provided by Mitsui Mining and Smelting Co. The zeta potentials of the slurry particles and the substrates were measured by electrophoresis and electroosmosis, respectively, to evaluate the electrical properties of the surfaces, using a LEZA-600 Laser Electrophoresis Zeta Potential Analyzer of Otsuka Electronics Co. The zeta potential of the particles and the plates were measured in 10^{-3} M KCl and 10^{-2}M NaCl solution, respectively. The zeta potential of the plates was measured using a proprietary

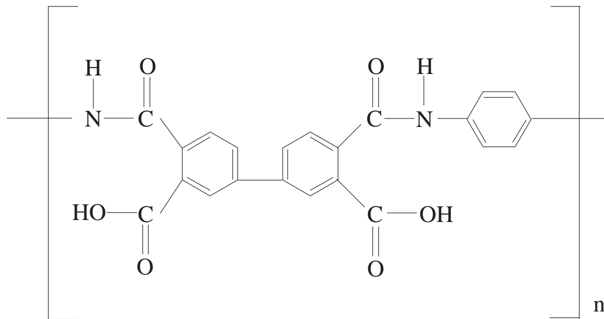


Fig. 1. Schematic chemical structure of PI2611, the polymide used for the experiment.

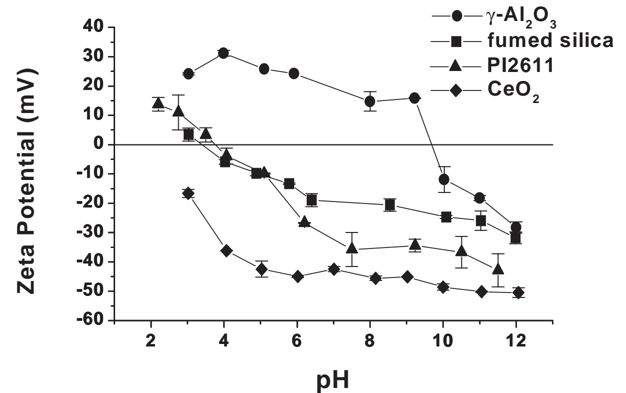


Fig. 2. Zeta potentials of the abrasives and polyimide surface used in the experiment.

monitor solution provided by Otsuka Electronics Co. Particle size was measured using ELS-8000 from Otsuka Electronics Co. The particles were dispersed in DI water and treated by ultrasound for 5 min before the particle size measurement. pH for the zeta potential and particle size measurements was adjusted by the addition of HCl and NaOH. Surface area analysis was performed using an Autosorb-1 from Quantachrome Co. using the BET method. Samples were out-gassed for 2 h before the measurements and N_2 was used as an adsorption gas at 110°C. The static contact angles of the PI surfaces were measured with the KRÜSS G10 Contact Angle Measurement System.

A Dap V mini polishing system of Struers was modified for the experiment. Polishing was optimized and performed for 5 min at a feeding speed of the slurry of 25 ml/min, head and plate speed of 145 rpm, and applied pressure of 3.22 psi. The Suba IV pad from Rodel was used for the polihsing.

The thicknesses of the polished samples were measured by both Dektak^3 from Veeco Instruments Inc. and NanoSpec from Nanometrics. Surface roughness was randomly measured at five points in each specimen by Dektak^3 under a 1000 μm scan length and 200 μm filtering condition.

3. Results and Discussion

The zeta potentials of the abrasives and the PI used in this experiment are shown in Fig. 2. As the pH increased, the zeta potentials decreased to negative values. The isoelectric points (IEPs) were measured to be 9.8 and 3.5 for γ-alumina and fumed silica, respectively. The IEP of ceria was not found in the measured pH range. The PI surface showed an IEP of 3.7. Measurement of the zeta potentials of the particles and surfaces is important to understand the dispersion of the particles in solutions and the adhesion of the particles on the surfaces. If the particles or surfaces had potentials with the same sign, they would repel and if they had opposite signs, they would attract each other due to the interaction of the electrostatic double layer forces created between them. Particles with a large absolute value of the zeta potential are more easily dispersed in solution than those near the IEP. It is clear from the measurements that ceria and fumed silica are stable in alkaline solutions and alumina in acidic environments. If the wafer surface and particles had the same sign of charges and large absolute values, the removal of particles from the wafer surface after polishing would be much easier. From the zeta potential measurements, it was expected that alkaline chemistry might be more suitable for formulating fumed silica and

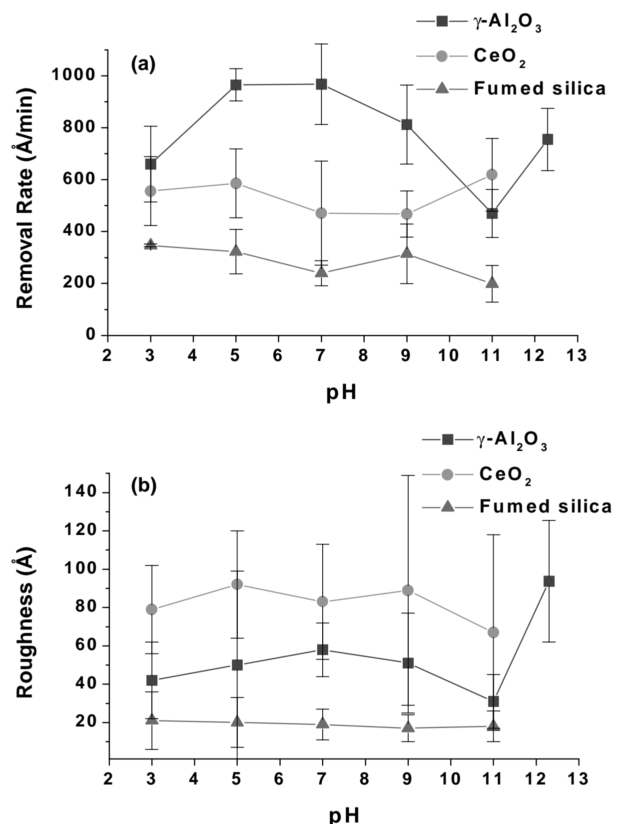


Fig. 3. Change of (a) the removal rate and (b) surface roughness of polyimide films as a function of the slurry pH at 0.5 wt% abrasive content.

ceria slurries and cleaning after PI CMP.

Figure 3 shows the removal rate and the surface roughness of PI after polishing with silica, ceria and alumina slurries as a function of the slurry pH. These slurries contained 0.5 wt% abrasives in DI water and their pHs were adjusted by the addition of HCl or NaOH. The alumina-based slurry showed the highest removal rate among the three slurries investigated. This might be attributable to the larger size and greater hardness of alumina particles. Tables I and II show the sizes of the particles in DI water at different pH and hardness values of the particles. Although both ceria and silica have similar hardness values, the ceria-based slurry showed a greater removal rate. In addition, there was no significant difference in the removal rates of silica and ceria slurries in the pH range investigated. However, both the highest and lowest

Table I. Particle sizes of abrasives used in the experiment at different pHs.

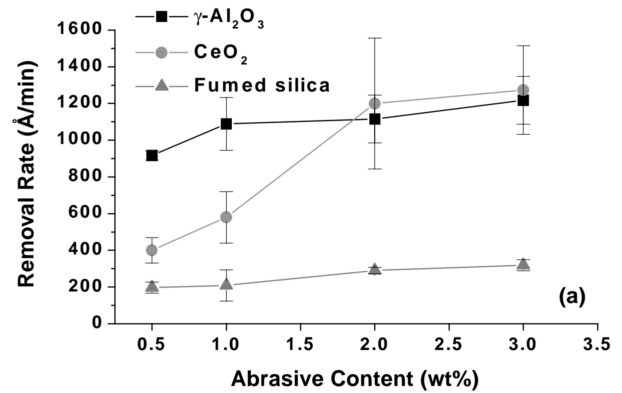
Particles	pH	Particle size (nm)	
		1st measurement	2nd measurement
Al_2O_3	3	736.3	707.5
	10	656.1	594.3
Fumed silica	2	414.1	484.0
	10	169.9	164.5
CeO_2	2	358.4	365.0
	3	376.8	366.6
	11.5	232.9	239.7

Table II. Hardness of the materials used in this study.[10)]

Materials	Hardness (Mho's scale)
Al_2O_3	8
CeO_2	6
SiO_2	6–7

Table III. Surface area of the abrasives used in the experiment.

Particles	Surface area (m^2/g)
CeO_2	14.22
Al_2O_3	86.61
Fumed silica	228.5



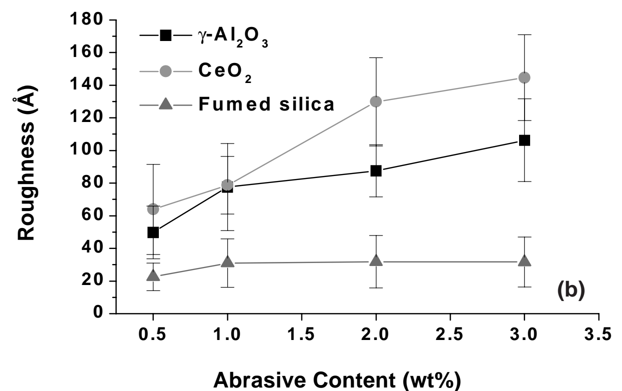


Fig. 4. Change of (a) the removal rate and (b) surface roughness of polyimide films as a function of the abrasive content in DI water only.

removal rates were measured when alumina slurry was used for PI CMP. The highest removal rates were observed in the pH range of 5 to 7. The lowest removal rate was observed at pH 11, but the rate increased again at higher pH values. It is not clear why the removal rate was markedly decreased at pH 11 but increased at pH 12.3. A similar result was reported in the case of Parylene CMP.[11)]

Surface roughness as shown in Fig. 3(b) was not exactly proportional to the removal rate but it was to the surface area of the particles. Use of ceria particles resulted in the highest surface roughness observed after the CMP. Table III shows the surface areas of the particles. Fumed silica particles showed the largest surface area and ceria particles the smallest. In order to reduce the surface defects such as the roughness and the scratches observed after polishing, it might be better to use particles with a larger surface area.

The particle content was varied from 0.5 to 3.0 wt% in DI water as shown in Fig. 4(a) in order to investigate the effect of particle content in the slurry on the removal rate. Alumina slightly increased the removal rate when particles were added up to 1 wt%; thereafter, the rate remained almost constant. Ceria increased the removal rate rapidly up to 2 wt% and the removal rate remained a constant thereafter. However, fumed silica showed an almost constant removal rate over the entire particle content range investigated, although there was a slight increase at higher particle contents. Surface roughness after polishing was proportional to the particle content in the case of ceria and alumina slurries as shown in Fig. 4(b). As discussed above, ceria particles also gave the highest surface roughness after PI polishing. Based on the measured removal rates and surface roughnesses, 0.5, 2 and 3 wt% of alumina, ceria and silica particles, respectively, were used in the slurry formulation for PI polishing.

Because the chemical etching of PI is an important procedure in the CMP process, the etch rate of PI was measured for various etchants at different concentrations and temperatures as shown in Table IV. The etch rate of PI was negligible at low temperatures for all the chemicals investigated. The etch rate of PI was higher in alkaline solutions. It is known that the imide rings on a PI surface form amic acid by reaction with OH^- in alkaline chemicals. The amic acid is further decomposed by hydrolysis and OH^- is known to enhance this reaction.[12)]

Among the chemicals investigated, TMAH and KOH were chosen for addition to the slurries to determine the effects of these chemicals on the removal rates. The changes in the removal rate and the surface roughness of PI are shown in Fig. 5 as a function of the slurry pH in the slurry containing 0.5 wt% alumina. Slurries containing 3 wt% TMAH (pH = 13.5) and KOH (pH = 13.4) showed removal rates of 922 and 775 Å/min, respectively. It was interesting to note that the removal rates with TMAH- and KOH-based slurries were very similar to that with a DI-water-based slurry. However, when the pHs of the TMAH- and KOH-based slurries were reduced to 10 and 7, respectively, by adding HNO_3, the removal rate decreased to a value lower than that with a DI-water-based slurry. The surface roughness was very dependent on the removal rates as shown in Fig. 5(b).

The removal rates of PI by a TMAH-based silica slurry are shown in Fig. 6 as a function of the pH. Except at pH 13, the removal rate increased with increasing pH but the increase was significantly lower than that with alumina slurry. The surface roughness was constant at around 30 Å and independent of the pH. The removal rate of PI by 2 wt% ceria-based

Table IV. The chemical etch rate of polyimide films at various chemical concentrations and temperatures.

(very small: <5 Å/min, small: <10 Å/min)

Chemicals	pH	Etch rate (Å/min) 25°C	50°C	85°C
HNO_3 (10 wt%)	0.56	0	very small	very small
NaOH (10 wt%)	12.7	0		
Ethylenediamine (10 wt%)	12.7	0	small	
Ethylenediamine (10 wt%)	11.9	0	very small	
KOH (5 wt%)	13.5	0	35	
KOH (10 wt%)	13.9	small	81	253
TMAH (0.5 wt%)	12.9		small	
TMAH (3 wt%)	13.5		19	
TMAH (5 wt%)	13.8	0	33	
TMAH (10 wt%)	14.2	small	130	913
TMAH (10 wt%) + HNO_3	12	1	small	
TMAH (10 wt%) + HNO_3	11		very small	
TMAH (2.5 wt%) + Ethylenediamine (2.5 wt%)	13.5		14	
TMAH (2 wt%) + Ethylenediamine (1 wt%)	13.3		15	

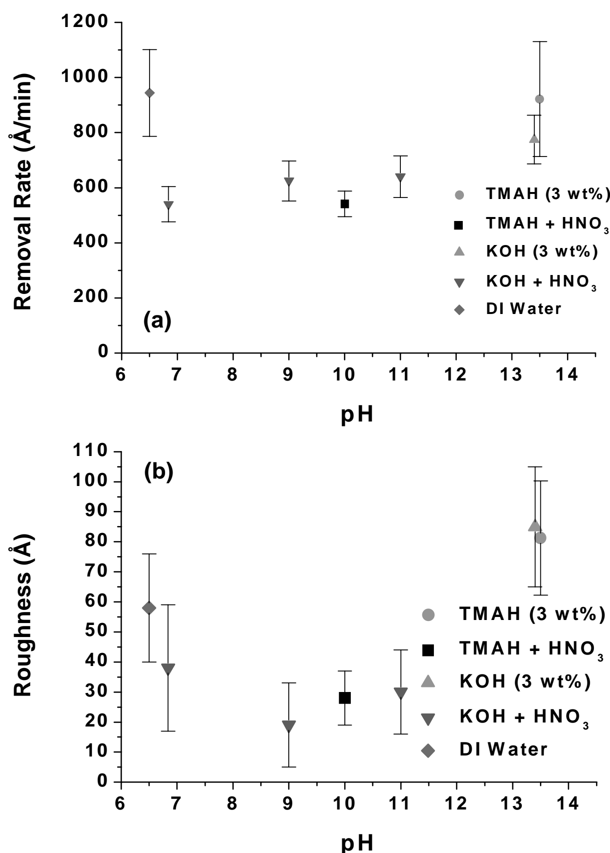


Fig. 5. Change of (a) the removal rate and (b) surface roughness of polyimide films as a function of the slurry pH at 0.5 wt% Al_2O_3 abrasive.

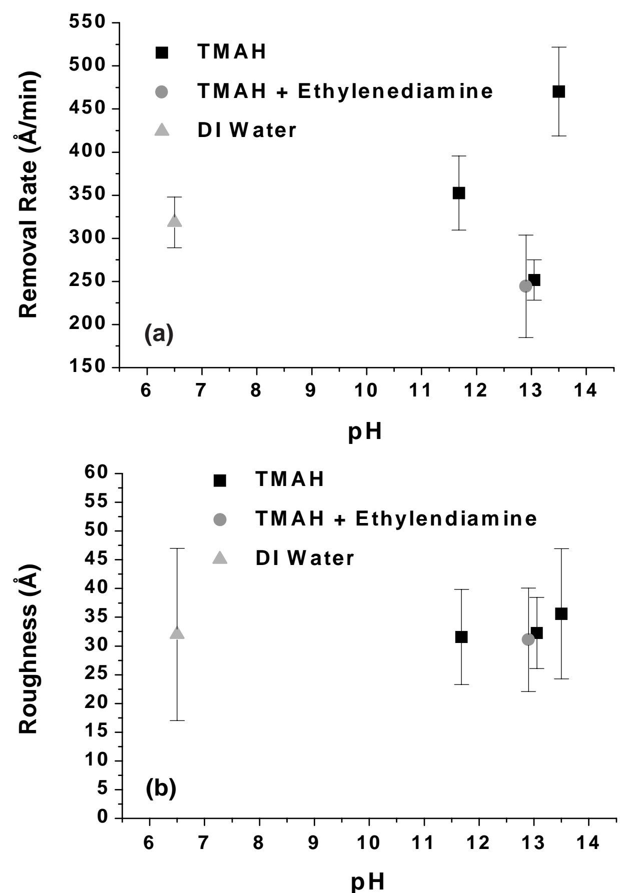


Fig. 6. Change of (a) the removal rate and (b) surface roughness of polyimide films as a function of the slurry pH at 3 wt% fumed silica abrasive.

slurry is shown in Fig. 7. The removal rates are strongly dependent on the pH of the slurry. When the pH was increased from 11.7 to 13.5, the removal rate increased from 1290 to 9300 Å/min. As discussed for the alumina slurry, dependence of surface roughness on the removal rates was also observed for the ceria slurry.

The addition of ethylenediamine in TMAH solution has been reported to increase the etch rate of PI[13,14]. The addition of 2 wt% ethylenediamine to 0.5 wt% TMAH-based ceria slurry did not increase the removal rate; on the contrary, a decrease of removal rate was observed. In addition, the soaking of PI in hot DI water was reported[15] to induce the PI to swell and thereby increase the etch rates in the chemicals. However, the presoaking of PI in DI water at 85°C did not increase the removal rate.

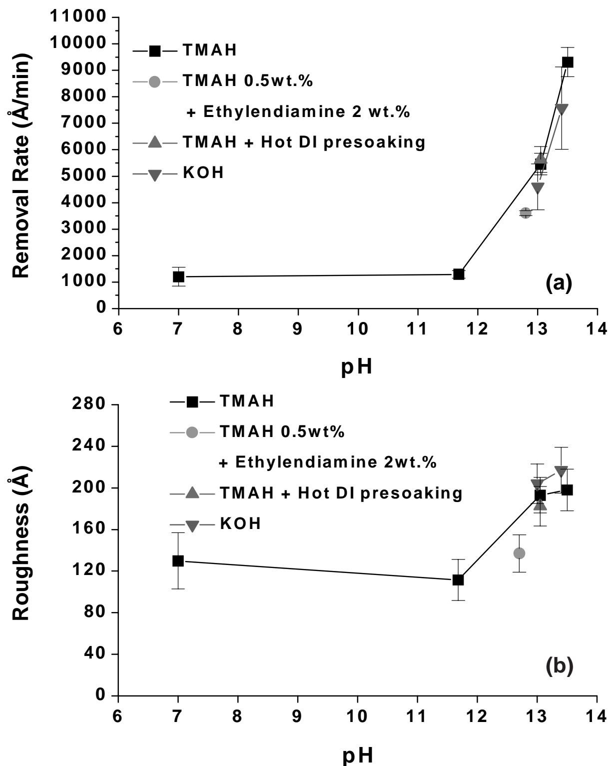


Fig. 7. Change of (a) the removal rate and (b) surface roughness of polyimide films as a function of the slurry pH at 2 wt% CeO_2 abrasive.

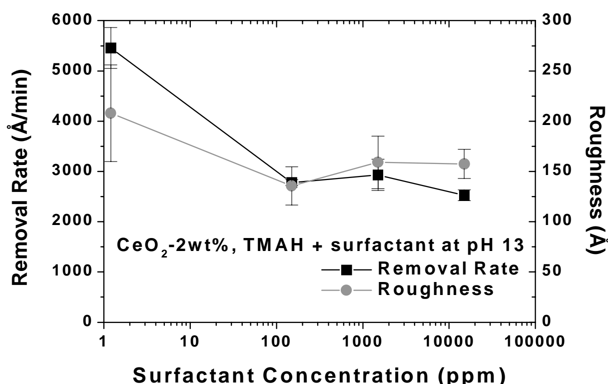


Fig. 8. Change of the removal rate and surface roughness of polyimide films as a function of the surfactant concentration in the slurry.

Surfactant was considered to increase the chemical reaction between slurry chemicals and the PI surface due to the increased solubility and wettability of polished materials.[16–18] The static contact angle of the slurry was measured to be between 70° and 79°, depending on the curing conditions on PI without the addition of surfactant to the slurry solution. The addition of Triton X-100 decreased the contact angle to 40° initially and then to below 10° in 5 min. Figure 8 shows the removal rate of PI as a function of the surfactant concentration in ceria slurry. A decrease in the removal rate was observed as the concentration of the surfactant increased. At its critical micelle concentration (CMC, 150 ppm), the removal rate was reduced to half of the rate observed in the absence of the surfactant. Hydroxide ions in the slurry are considered to attack imide rings and cut the chain, then weaken the PI bond at the surface enhancing the etch rate of PI and hence the removal rate at high pH. Mechanical abrasion during CMP enhances the removal rate of PI. However, the adsorption of surfactant at the polyimide surface may disturb the chemical attack of PI by OH^-[19] thus resulting in the reduction of the etch rates, and thereby the removal rates.

4. Conclusions

Zeta potentials of particles and PI were measured to prepare slurries and to minimize the surface contamination induced by electrostatic double layer interaction. Alkaline solutions might work better for formulating silica and ceria slurries and cleaning after PI CMP due to the large negative zeta potentials of these substance in the alkaline pH region. For the highest removal rate and lowest surface roughness, 0.5, 2 and 3 wt% of alumina, ceria and silica particles, respectively, were used for the PI polishing. The highest removal rates of PI were observed for alumina slurry when the particles were dispersed in DI water. Silica slurry showed the lowest removal rate. Ceria particles yielded the highest surface roughness after the CMP. The removal rate was proportional to the size and hardness of the particles used in the slurries. However, the surface roughness was related to the surface area of the particles; the greater the surface area of the particles, the smoother the surfaces. The etch rate of PI in acidic and alkaline solutions was negligible at room temperature. In alkaline solutions, an increase in the etch rate was observed at higher temperatures due to the attack of PI surfaces by OH^-. When TMAH was added to the slurries, ceria slurry showed the highest removal rate of PI. The removal rates were strongly dependent on the pH and increased from 1290 to 9300 Å/min when the pH was increased from 11.2 to 13.5. The addition of ethylenediamine to the TMAH solution and the soaking of PI in hot DI water did not increase the removal rate during CMP. The addition of surfactant decreased the removal rates to half of the rate observed in the absence of surfactants.

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