



Controlling Germanium CMP Selectivity through Slurry Mediation by Surface Active Agents

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New developments and device performance requirements in microelectronics industry add to the challenges in chemical mechanical planarization (CMP) process. One of the recently introduced materials to semiconductor manufacturing is germanium which enables improved device performance through better channel mobility in shallow trench isolation (STI) applications for advanced circuits. This paper focuses on controlling germanium/silica selectivity for advanced STI CMP applications through slurry modification by surface active agents. Surface adsorption characteristics of cationic and anionic surfactants on germanium and silica wafers are analyzed in order to control selectivity as well as the defectivity performance of the CMP applications. The effects of surfactant charge and concentration (up to self-assembly) are studied in terms of slurry stability, material removal rates and surface defectivity. Surface charge manipulation by the surfactant adsorption on the germanium surface is presented as the main criteria on the selection of the proper surfactant/oxidizer systems for CMP. The outlined correlations are systematically presented to highlight slurry modification criteria for the desired selectivity results. Consequently, the paper evaluates the slurry selectivity control and improvement criteria for the new materials introduced to microelectronics applications with CMP requirement by evaluating the germanium silica system as a model application.

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Microelectronics industry has been driven by silicon based CMOS devices until the recent advances in nano-scale transistor device development demanded new materials and processing innovations to enable the scaling down and to overcome the physical limitations within the currently used technologies. Germanium is being used as a substitute for silicon as the new channel material for forthcoming MOSFET devices due to its high mobility of charge carriers (three times higher than in Si for electrons and four times for holes).^{1,2} During the fabrication process of deep-scaled Ge channel metal oxide field effect transistors (MOSFETs), Ge is epitaxially grown on Si in SiO₂ trenches following the conventional STI process. This integration method results in a very rough surface finish and hence chemical mechanical planarization (CMP) is used to planarize the surface to expose the silica/germanium interface enabling the device fabrication. CMP performance has to be controlled by the design of effective slurry compositions including the chemical composition and abrasive particle selection to enable selectivity of Ge versus silica while maintaining slurry particle stability for minimal defectivity. Therefore, advanced slurry formulations are needed for Ge CMP applications for an optimized planarization performance.³⁻⁵

Recent investigations on Ge CMP have outlined some of the fundamental aspects of the process requirements. It has been shown that slurries containing colloidal and fumed silica particles along with hydrogen peroxide (H₂O₂) as an oxidizer were effective in polishing Ge. The material removal rates (MRR) and dissolution rates (DR) in the basic pH region were observed to be higher than those in the acidic pH regions both for the Ge and SiO₂.^{6,7} However, the presence of H₂O₂ at high concentrations resulted in pitting on Ge wafers and the chemically promoted dissolution resulted in very high Ge removal rates. From the device performance standpoint, a slightly recessed oxide profile was reported to be needed for better performance suggesting that a slightly higher silica removal rate is preferred at the SiO₂/Ge interface.⁸ To inhibit the dissolution of Ge, a 16 carbon chain CTAB

surfactant at 0.1 mM and pH 8 was used and observed to help control the Ge removal rate (~450 nm/min) enabling some control on selectivity.⁸

Another critical aspect in CMP is the quality of the surface finish to accomplish defect free device manufacturing. Hence, slurry stabilization is required to effectively planarize the surface with a minimum surface roughness and defectivity. Previously, we have established that alkyl quarternary amine mediated silica nanoparticle dispersions are able to meet the stringent stability criteria necessary in critical CMP operations.⁹ However, the presence of strongly adsorbed surfactant structures at the solid-liquid interface resulted in negligible material removal rates. Adjustment of pH and ionic strength were adopted to initiate appreciable friction and material removal rates in silica polishing systems containing dodecyl trimethylammonium bromide (C₁₂TAB) based dispersants.¹⁰

A similar approach has been implemented in this study to accomplish necessary slurry selectivity with higher silica removal rate while maintaining the slurry stability that provides minimal surface deformation. Both anionic (sodium dodecyl sulfate-SDS) and cationic C₁₂TAB micelles were used in the slurry formulations as a function of pH and oxidizer concentration. CMP performances of Ge and SiO₂ wafers were evaluated in terms of material removal rates, selectivity and surface quality. Initially, the baseline Ge and SiO₂ CMP were studied to optimize the oxidizer concentration and pH of the slurry systems. Based on the minimum amount of the H₂O₂ concentration determination, slurry stability in the presence of oxidizer with and without the surfactant addition was investigated. Once stable slurries were obtained, surfactant adsorption characteristics were studied through surface charge measurements. It was observed that the surfactant structures can help obtain selectivity on the silica/germanium system at 0.25× critical micelle concentration (CMC) with better surface performances obtained by anionic SDS surfactant.

Materials and Methods

Preparation and characterization of the CMP slurries.— CMP slurries were prepared by using fume-silica powder obtained from

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Sigma-Aldrich by stabilizing the silica particles at 3wt% solids concentration in pH adjusted DI water through ultrasonication. Baseline slurries were prepared at pH 9 initially for adequate dispersion followed by pH adjustment through addition of KOH or HCl as needed to obtain slurry pH of 2, 6 and 11. In order to monitor the dispersion and stability characteristics of the slurries, particle size analyses were performed via light scattering technique using Coulter LS 13-320 Laser Diffraction Particle Size Analyzer (Beckman Coulter ALM-aqueous Liquid Module). The background water used to run the size analyses measurements was prepared to have the same pH as the measured slurry pH to be able to keep the suspensions stable during the measurements and prevent the local pH shock related agglomeration.

In order to increase the CMP removal rates, H_2O_2 was added into the slurries as an oxidizer at an optimized concentration of 0.1M based on optimization in our earlier work.¹¹ As it is known H_2O_2 is not stable at room temperatures. Hence it was prepared and introduced as secondary slurry during CMP on the Tegramin polisher system. This approach also helps in preventing the silica slurry agglomerating and settling in the slurry form. $C_{12}TAB$ and SDS surfactants were added into the slurries at quarter ($0.25\times$) CMC, ($1\times$) CMC and ($2\times$) CMC concentrations. These values are 4 mM, 16 mM and 32 mM for $C_{12}TAB$ surfactant and 2 mM, 8 mM and 16 mM for the SDS surfactant, respectively.⁶ In order to create stable micelles, concentrations up to $2\times$ CMC were evaluated. All the chemically modified slurries were analyzed for the particle size distributions for checking their stability responses.

The zeta potentials of the prepared slurries were measured as a function of pH before and after surfactant addition by using Malvern ZS Zeta-sizer. The surface charges were found to be corresponding to the surfactant mediation turning positive in the presence of the cationic $C_{12}TAB$ surfactant and negative in the presence of the anionic SDS surfactant.

Material removal rate analyses.— Material removal rates of the Ge/SiO₂ system were measured by evaluating the dissolution rates in addition to CMP application. Figure 1 shows the experimental set-up used for the dissolution rate evaluations and the CMP experiments. Removal rate analyses were conducted on bare n-type Germanium wafers with 2" diameter and 400 μm Ge thickness obtained from University Wafers and 6000 \AA thick high density plasma (HDP) deposited SiO₂ wafers donated by Texas Instruments Inc. HDP deposited silica was intentionally selected for this study to be able to best represent the commercial STI CMP applications since it is the standard industry choice for the nodes where the Ge is implemented for the semiconductor manufacturing. All the wafers were cut to 16×16 mm coupons for material removal rate analyses.

Dissolution rate analyses.— Ge and HDP SiO₂ wafer coupon dissolution rates were measured in a glass beaker containing 100 mL of the etchant solution. Each coupon was initially weighed on a PRECISA 360 ES scientific balance with 0.01 mg accuracy. The solution was stirred using a magnetic stirrer at 300 rpm rotational speed at room temperature and the wafer coupons were retained for 1 min in the solution. In order to prevent the dissolution of the whole wafer, a special experimental set-up was designed as illustrated in Figure 1a. The wafer coupon was attached to the holder made of teflon and exposed only on the top side to the dissolution solution. This approach prevents the isotropic static etch of the wafer and hence can correctly measure the dissolution rate of the relevant surface. After the coupons were removed from the solution, they were washed repeatedly with deionized (DI) water, dried in a nitrogen stream and reweighed. The weight loss was used to calculate the dissolution rate and the reported rates were obtained by averaging over three experiments.

CMP analyses.— CMP experiments were conducted on Tegramin-31 table-top polisher by using standard K-groove SUBAIV-IC1000 stacked polishing pad. Figure 1b shows the experimental CMP set-up with the wafer coupon holder. The down force was set to 30 N (16.4 psi) on the 1.6×1.6 cm wafer coupons with 150 rpm rotational ve-

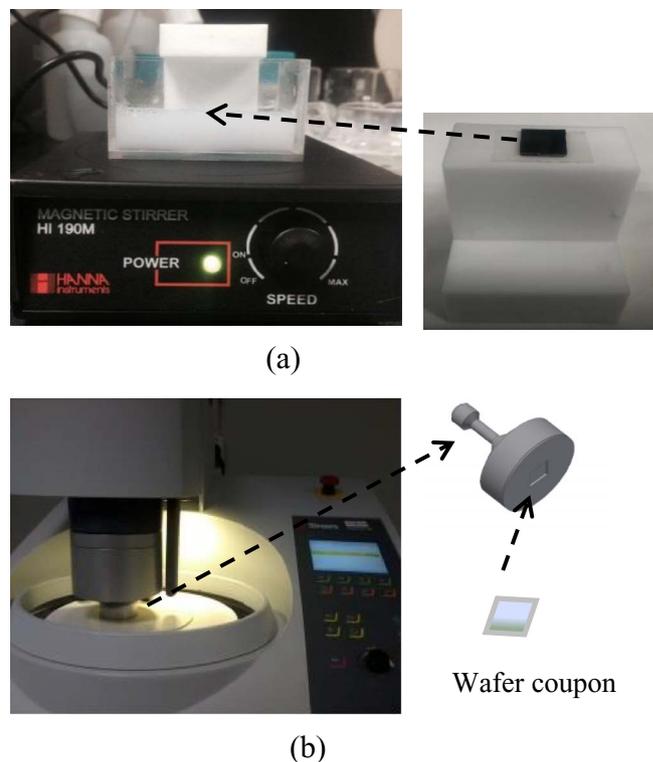


Figure 1. Experimental set-up for (a) one-sided dissolution rates analyses conducted by attaching the wafer on a special holder to expose only the top side to the slurry while the slurry is stirred simultaneously and (b) desk-top chemical mechanical planarization tool in operation.

locity and 25 ml/min slurry flow rate. The material removal rates were determined from the difference in the weights of the wafer coupons before and after CMP measured by the PRECISA 360 ES balance. Both Ge and HDP SiO₂ material removal rates were averaged from minimum 3 experiments. Post CMP, wafers were rinsed and ultrasonicated in DI water adjusted to pH 9 and dried with nitrogen gas and maintained in a desiccator prior to surface quality testing.

Surface morphology and charge measurements.— **Surface roughness analyses.**— Surface roughness analyses were performed by Nanomagetics Instruments atomic force microscope (AFM) before and after polishing. Three measurements were performed per sample close to the center of the wafer coupons by $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ scans and root mean square (RMS) roughness values were reported as an average with standard deviations.

Surface charge measurements.— An electrokinetic analyzer (SurPASS, Anton Paar GmbH) was used to measure the surface charge of the germanium and SiO₂ surfaces as a function of surfactant concentration. The wafers were attached to both sides of an adjustable-gap cell and separation distance between the two wafer surfaces was set to approximately 100 μm . DI water was flown through the cell with 1 mM KCl solution as the background electrolyte by ramping the differential pressure from 0 to 400 mbar in both flow directions. The surface charge was measured at pH 6 and also the zeta-potentials were determined from the Smoluchowski equation by measuring the change in streaming current versus the applied differential pressure.

Results and Discussion

Baseline selectivity evaluations on the SiO₂/Ge system.— The preliminary evaluations on the Ge and SiO₂ wafers were started by analyzing the dissolution rates of the wafer coupons as a function of pH in DI water. Dissolution rate tests were conducted on both germanium and silica wafers as a function of pH (at 2, 6 and 11) in

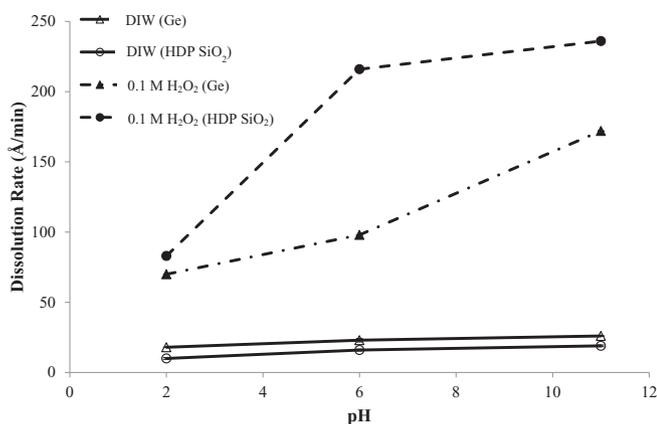


Figure 2. Dissolution rate analyses on Ge and HDP deposited SiO₂ wafer coupons as a function of pH in DI water at 25°C in the absence and presence of 0.1 M H₂O₂ as an oxidizer.

the presence and absence of 0.1 M H₂O₂ in the solution. Figure 2 illustrates the dissolution rates obtained at pH 2, 6 and 11 for which both germanium and silica have shown increasing dissolution rates as a function of pH. The dissolution rates were limited to ~20–25 Å/min in the absence of the oxidizer and when 0.1 M of H₂O₂ was added, dissolution rates increased considerably (up to 10 times) with the best separation in the dissolution rates between the Ge and SiO₂ observed at pH 6. The increase in the dissolution rate of the HDP oxide is rather unexpected. However, it is known that hydrogen peroxide dissociates into H₂O and O₂ in water. Simultaneously, silica surface dissolves due to the attack of the negatively charged non-bridging oxygen atom by the solvated hydrogen ion (H₃O⁺) in the water.¹² Hence it is plausible that the presence of H₂O₂ enhances the silica dissolution rate based on the promoted level of oxygen acting as a catalyst for attack by water on the silica network. In addition, the properties of the HDP deposited oxides are known to be different from the thermally grown oxides with 1.6 to 1.8 times higher wet etch rate on the HDP oxide.¹³ Therefore, dissolution of the HDP oxide films in the H₂O₂ solutions are also expected to be higher as compared to the typical thermally grown oxides. This behavior also highlights the challenges in providing selectivity in CMP of Ge against HDP SiO₂. Furthermore, this observation better justifies the selection of the HDP oxide in this study instead of using thermally grown oxides for the pilot tests in the microelectronics applications. HDP oxide is preferred in STI deposition since it enables the proper gap fill by continuous etch/deposition cycles taking place in the deposition process to prevent voids in the STI trenches.

In order to verify the effect of pH on CMP selectivity, a similar analyses was conducted on the wafers by running CMP tests in the presence of 0.1M H₂O₂ in the slurries. As mentioned in the Materials and methods section, H₂O₂ solution was fed to the polisher as secondary slurry during the CMP experiments. Figure 3 shows the MRR responses obtained at pH 2, 6 and 11 on Ge and HDP SiO₂ wafers. In parallel to the dissolution rate analyses, the best separation in between the MRR values was obtained at pH 6 and the SiO₂/Ge selectivity values of 2.53, 3.00 and 2.66 were obtained at pH 2, 6 and 11, respectively. Therefore, the rest of the studies were conducted by adjusting the slurry to pH 6 to obtain the highest selectivity. Furthermore, it was intended to limit the chemical dissolution of Ge at the high pH values demonstrated in Figure 2 in addition to the earlier observations in the literature.³ The low pH range was also avoided since the isoelectric point of SiO₂ is at ~pH 2.3 for the silica particles used as abrasives in the slurry preparation. Hence pH 6 was optimized for the slurry preparation.

Once the selectivity was achieved through MRR evaluations, it was also critical to evaluate the surface quality response of the wafers polished at pH 6 in the presence of 0.1 M of H₂O₂. It is known that

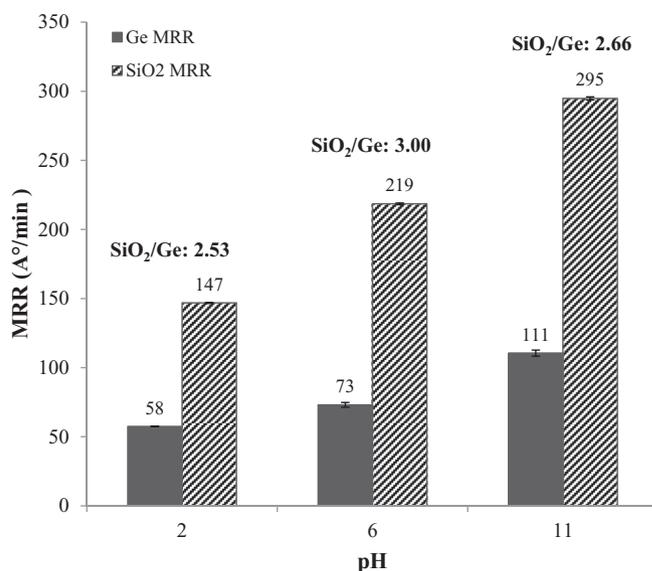


Figure 3. Material removal rate responses on Ge/SiO₂ as a function of pH with 0.1 M H₂O₂ in silica based CMP slurry.

the addition of oxidizer tends to agglomerate the oxide based slurry. Figure 4 compares the particle size distribution measurements of the fume silica slurries prepared at pH 2, 6 and 11 with and without the addition of H₂O₂. As it can be seen on Figure 4a, the number percent particle size distribution analyses of the fume silica slurry in the absence of the oxidizer shows a mean particle size of 0.08 μm with a tail extending up to 0.4 μm at pH 11 and to 0.6 μm at pH 2 and 6. It is known that the best slurry stability can be reached through electrostatic repulsion at high pH on silica due to increased ζ-potential of the slurry particles. Hence the slurries prepared at pH 2 and 6 demonstrate a size distribution with a more pronounced tail at the larger size fraction. The presence of the larger tail is typical of the slurries prepared with the fume silica particles.¹⁴ Regardless of the selected pH, when the H₂O₂ is added into the slurries at 0.1 M, the mean particle sizes shifted up. Figure 4b illustrates the shift in the slurry particle size at pH 6, which is selected to be the best pH value to enable the best CMP selectivity.

Figure 5 illustrates the AFM micrographs of the Ge and silica wafers polished with the baseline slurry at pH 6 and the slurry after addition of the 0.1 M oxidizer simultaneously during the CMP. It can be seen that the surface quality of both types of wafers degraded in the presence of the oxidizer due to slurry agglomeration and residual particles. RMS roughness values increased significantly on the Ge wafers from 1.15 nm in the absence of the oxidizer to 2.65 nm in the presence of the oxidizer. These values were 0.79 nm and 1.1 nm on the silica surface with a surface particle created scratch noticed on the AFM micrograph. Consequently, it is needed to improve the slurry stability to improve the post CMP surface quality and analyze further improvement in the selectivity response of the Ge versus silica surface in the presence of surfactants.

Effect of surfactant mediation on selectivity of SiO₂/Ge system.— Modification of the CMP slurries through surfactant mediation is a common application to promote (i) stability, (ii) adjust removal rates and the related selectivities through modifying the abrasive particle/surface interactions^{9,10} and by limiting the dissolution rates,⁸ and (iii) to improve the surface quality of the wafers post CMP treatment. The main motivation of the use of surfactants in this study for the Ge CMP applications remain the same with an additional emphasis on systematically analyzing the effect of the surfactant charge and concentration on the CMP responses.

Figure 6 shows the isoelectric points (iep) of the Ge and HDP deposited SiO₂ wafers measured by the SurPass electrokinetic analyzer.

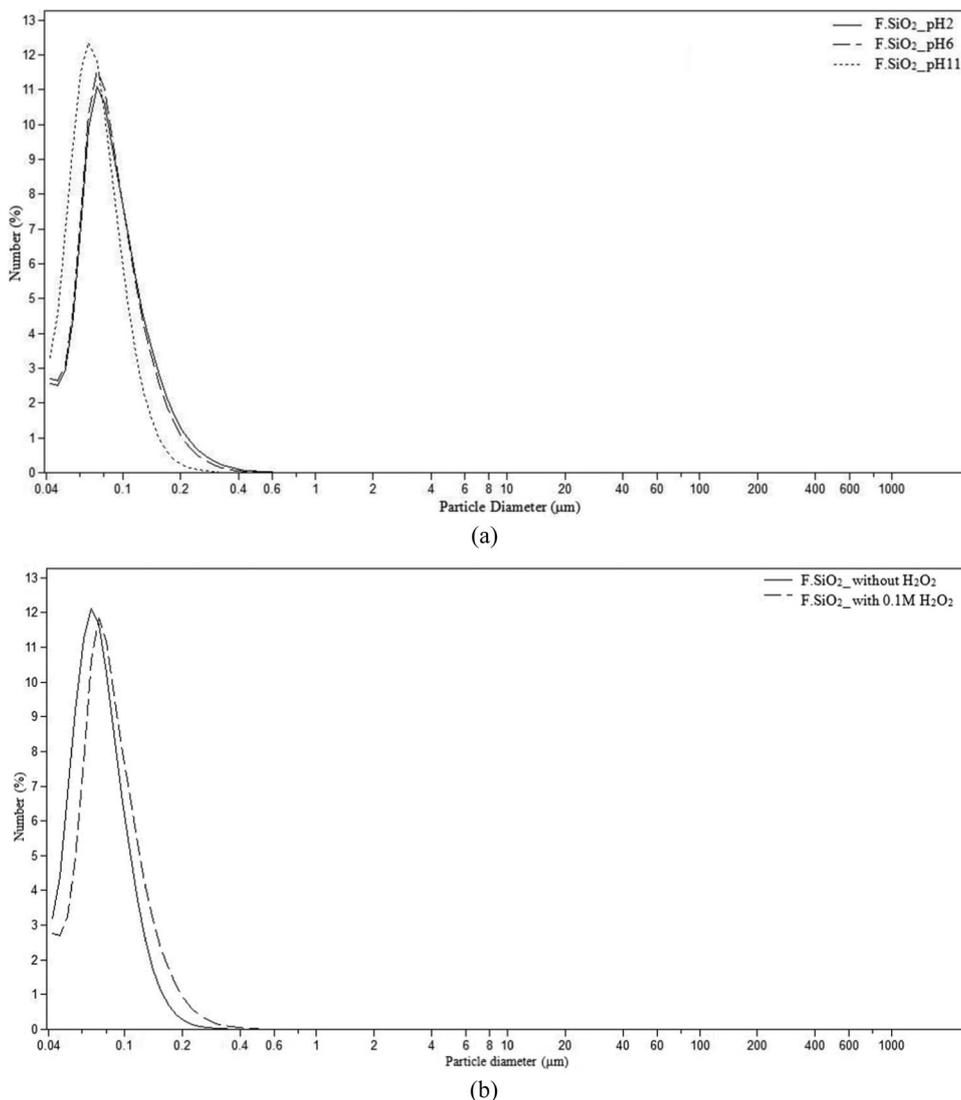


Figure 4. (a) Particles size distribution of 3 wt% fume silica based CMP slurry measured at pH 2, pH 6 and pH 11 and (b) Comparison of the particle size distributions of the CMP slurries before and after addition of 0.1 M H₂O₂ at pH 6.

It can be seen that the iep of the Ge is at pH 3.5 and HDP deposited SiO₂ is at pH 2.3. Therefore, it is expected that the silica surface is more negatively charged at pH 6 as compared to Ge and hence can adsorb a higher number of the cationic C₁₂TAB surfactant. In the case of the negatively charged surfactant SDS, however, due to the repulsion between the surfactant structures and the surface less surfactant adsorption is expected. Figure 7 illustrates the proposed mechanism of the surfactant adsorption for the bi-layer formation of C₁₂TAB and SDS at 0.25×CMC.

In order to evaluate the proposed adsorption mechanism, surface charge analyses were conducted on the Ge and SiO₂ wafer by using both surfactants at 0.25×CMC, 1×CMC and 2×CMC dosages at pH 6. Figure 8a shows the surface charge measurements on the Ge surface and Figure 8b shows the surface charge measurements on the HDP deposited silica surface. On both systems, addition of the cationic surfactant changed the baseline surface charges from negative to a positive value. This can be attributed to the relatively high concentration of the surfactant addition (4 mM for 0.25× CMC, 16 mM for 1× CMC and 32 mM for the 2× CMC) resulting in bilayer formation on the surface as demonstrated in Figure 7 schematically. Hence the -20 mV surface charge of the Ge wafer changed to ~30 mV at 0.25× CMC, ~40 mV at 1×CMC and ~45 mV at 2×CMC of the C₁₂TAB addition. At the high concentrations, the adsorption

of the surfactant to the wafer surface is also known to be driven by the surface affinity of the surfactants rather than the sole electrostatic interactions in the proposed adsorption mechanism presented in Figure 7.⁶ Consequently, even the negatively charged SDS surfactant adsorbs on the Ge surface appreciably, increasing the -20 mV baseline surface charge to -40 mV at 0.25× CMC, ~50 mV at 1×CMC and ~55 mV at 2×CMC (2 mM, 8 mM and 16 mM SDS addition, respectively).

When the surface charge values were measured on the HDP oxide surfaces (as shown in Figure 8b), however, at the low concentration of the surfactant (only 0.25 CMC) the baseline surface charge of the -58 mV changed to +18 mV with 4 mM of C₁₂TAB, and -50 mV with 2 mM SDS addition. Hence, it can be concluded that the electrostatic interactions play a more dominant role on the silica surface at the low concentration of the surfactants as illustrated in Figure 7.⁶ Yet, when the CMC is reached, the surface affinity of the surfactants take over as the adsorption mechanism. The reason why the Ge surface is more dominant in adsorbing surfactants through surface affinity can be explained by the hydrophobic nature of the Ge dominating the hydrophobic/hydrophobic interactions between the surfactant and the wafer surface.¹⁵ As an example, while the measured surface charge of the Ge increased from -20 mV to -45 mV in the presence of SDS micelles at 2× CMC (which is more than twice), the surface charge

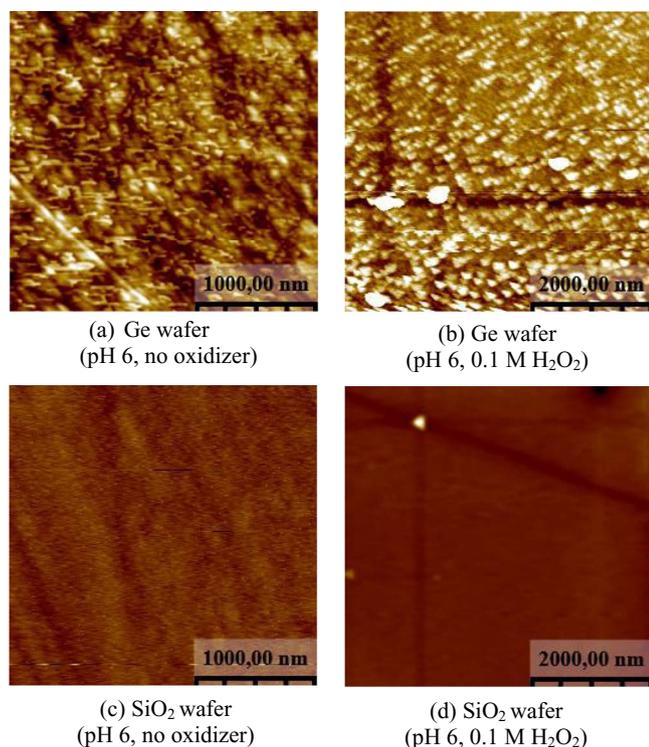


Figure 5. AFM characterization of the germanium and HDP deposited SiO_2 wafer surfaces after CMP application with 3 wt% fumed silica without H_2O_2 and with H_2O_2 at pH 6 for surface roughness responses. (a) Ge wafer polished at pH 6 without oxidizer, (b) Ge wafer polished at pH 6 in the presence of 0.1 M H_2O_2 , (c) SiO_2 wafer polished at pH 6 without oxidizer, (d) SiO_2 wafer polished at pH 6 in the presence of 0.1 M H_2O_2 .

on silica has only increased from the baseline value of -55 mV to -65 mV when the SDS micelles were added.

In addition to the evaluation of the surface charges of the wafers, the change in the ζ -potential of the silica particles in the CMP slurry was also evaluated as a function of the surfactant mediation by Malvern Zeta-sizer. Figure 9 illustrates the baseline silica slurry had -30 mV surface charge which again changed to positive values in the presence of cationic C_{12}TAB surfactant and became more negative in the presence of the anionic SDS surfactant. The relative absolute charge of the particles were much lower with the cationic surfactant (maximum of $+15$ mV with 32 mM C_{12}TAB) as compared to the SDS surfactant (maximum of -45 mV with 16 mM SDS). This observation led us

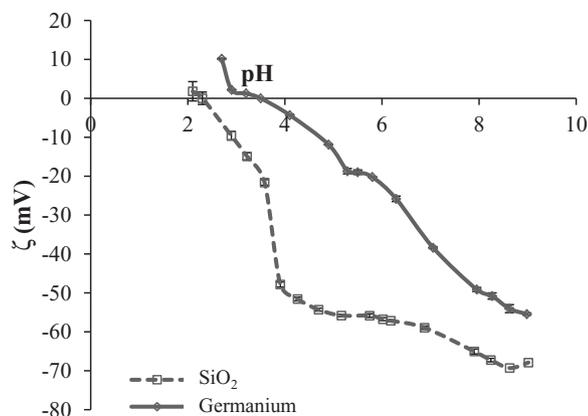


Figure 6. Iso-electric point determination on Ge and HDP SiO_2 wafers by surface charge measurement as a function of pH.

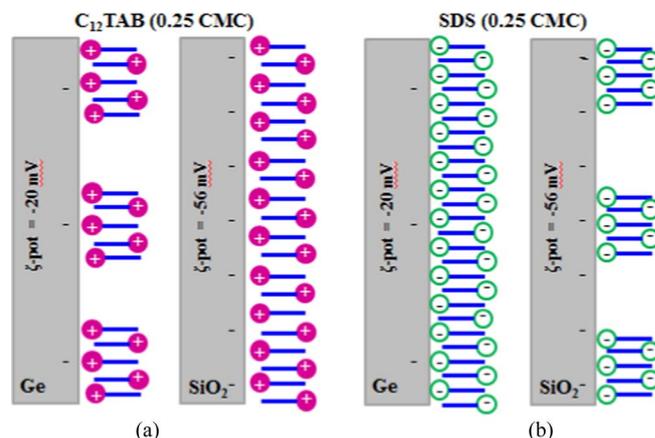


Figure 7. Schematic illustration of the hypothetical self-assembled surfactant adsorption on the Ge and silica wafers based on surface charge measurements at pH 6 (a) in the presence of C_{12}TAB at 32 mM concentration ($2\times\text{CMC}$) and, (b) in the presence of SDS at 16 mM concentration ($2\times\text{CMC}$).

to analyze the particle size distribution and the stability of the CMP slurry after the surfactant mediations.

Table I summarizes the particle size measurements of the slurries prepared by the C_{12}TAB and SDS surfactants at 0.25, 1 and $2\times\text{CMC}$ concentrations. It can be seen that, the slurries prepared by C_{12}TAB have shifted to much larger mean particle sizes at and above the CMC concentrations indicating severe agglomeration and destabilization of the slurry. Indeed, we observed that the baseline slurry tends to gel in the presence of C_{12}TAB when the H_2O_2 is added as an oxidizer.

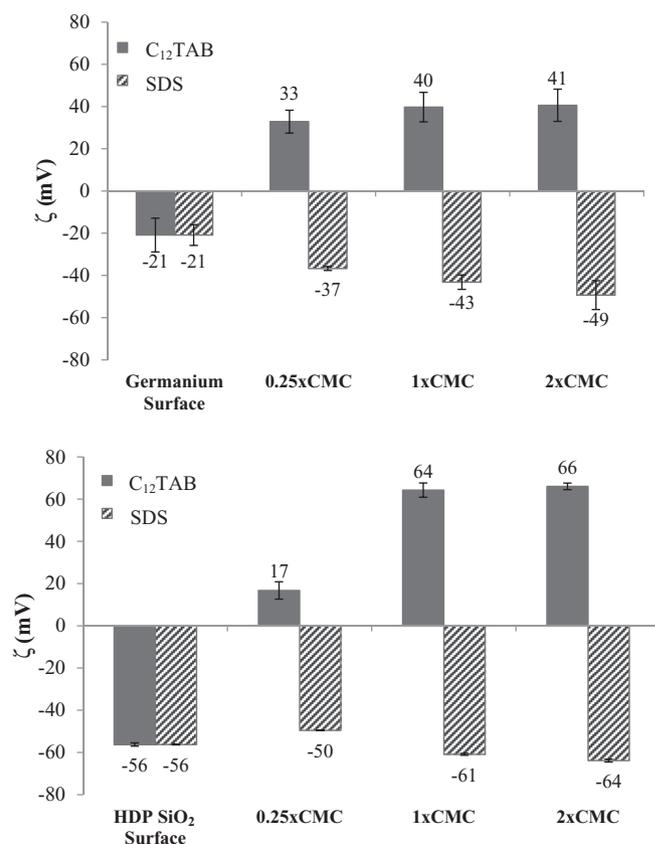


Figure 8. Zeta potential (ζ) measurements on (a) Ge wafer surface and (b) HDP SiO_2 wafer surface measured in 1 mM KCl solution as a function of surfactant concentration at pH 6.

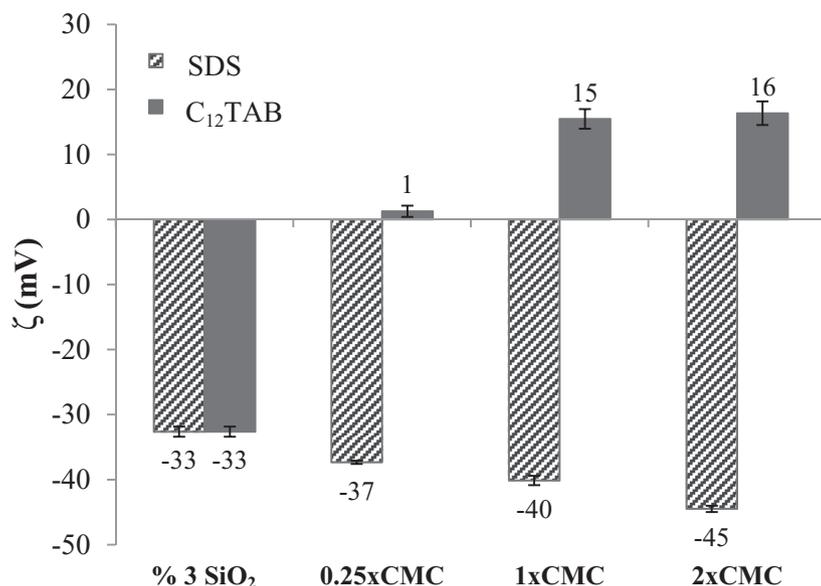


Figure 9. ζ -potential of fume silica based CMP slurry in the presence of $C_{12}TAB$ (0, 4, 16, 32 mM concentrations) and SDS (0, 2, 8, 16 mM concentrations).

Table I. Mean particle size of 3 wt% fume silica slurry as a function of surfactant concentration at pH 6.

$C_{12}TAB$	4 mM (0.25×CMC)	16 mM (1×CMC)	32 mM (2×CMC)
Mean particle size (nm)	98	12.3×10^3	11.7×10^3
SDS	2 mM (0.25×CMC)	8 mM (1×CMC)	16 mM (2×CMC)
Mean particle size (nm)	93	94	76

This behavior was also reported in the literature with an increased potential of gel formation with the increasing concentration of $C_{12}TAB$ particularly beyond CMC.¹⁶ Therefore, it is expected that although the cationic surfactant may help with the slurry selectivity, the surface quality would degrade which is not desired. In the presence of SDS on the other hand, the baseline mean particle size was observed to be maintained with a slight shift toward lower mean size indicating better stability obtained at pH 6 particularly at 2×CMC concentration in parallel with earlier literature findings.¹⁷

Based on the surface charge measurements on the wafers and stability testing of the CMP slurry in the presence of surfactants, CMP tests were performed to analyze the material removal rate, SiO_2/Ge selectivity and surface quality responses. Table II summarizes the material removal rates obtained on the silica and germanium surfaces as a function of the $C_{12}TAB$ and SDS concentrations. In all the evaluations, 0.1 M H_2O_2 was used as the oxidizer in the slurries. It can be seen that both systems were able to provide selectivity as required by

Table II. Material removal rate responses of the Ge and SiO_2 wafers as a function of $C_{12}TAB$ and SDS concentration.

$C_{12}TAB$	4 mM (0.25×CMC)	16 mM (1×CMC)	32 mM (2×CMC)
Germanium MRR ($\text{\AA}/\text{min}$)	787	1605	1196
HDP SiO_2 MRR ($\text{\AA}/\text{min}$)	3718	2158	1237
SiO_2/Ge Selectivity	4.7	1.3	~1.0
SDS	2 mM (0.25×CMC)	8 mM (1×CMC)	16 mM (2×CMC)
Germanium MRR ($\text{\AA}/\text{min}$)	873	997	1221
HDP SiO_2 MRR ($\text{\AA}/\text{min}$)	3120	1435	1474
SiO_2/Ge Selectivity	3.6	1.4	~1.2

providing a higher removal rate on silica as compared to germanium. Moreover, the SiO_2/Ge selectivity values of 4.7 and 3.6 were obtained at the quarter CMC concentrations of $C_{12}TAB$ and SDS surfactants, respectively. These values were higher as compared to the selectivity value of 3 achieved by using the baseline slurry at pH 6 without addition of surfactants. As the concentrations of both surfactants were increased, the selectivity decreased. This trend can be explained by (i) the reduced frictional interactions in the presence of self-assembled surfactant structures in the slurry^{10,18} and (ii) the limited dissolution reaction at the higher concentrations of the surfactants as observed in the literature earlier.⁸ Table III lists the dissolution rates measured with $C_{12}TAB$ and SDS. The general tendency is toward decreasing dissolution rates by increasing surfactant concentrations which is in line with the measured surface charge results on the Ge and silica surfaces given in Figure 8. The more surfactant molecules are attached on the surface, the less is the rate of dissolution on both the cationic and the anionic surfactant addition. The fact that the dissolution rates are higher on both the germanium and the silica surface in the presence of surfactants as compared to using only hydrogen peroxide can be explained by the tendency of surfactants forming complexes in the presence of hydrogen peroxide.¹⁶ It is also worth noting that the material removal rate responses are very similar to the dissolution rates at the quarter CMC concentration of both surfactants on the Ge surface. In the presence of 0.25× $C_{12}TAB$, the MRR is 787 $\text{\AA}/\text{min}$ while the dissolution rate is 709 $\text{\AA}/\text{min}$. Similarly, in the presence of 0.25× CMC of SDS, the MRR is 873 $\text{\AA}/\text{min}$ while the dissolution rate is 616 $\text{\AA}/\text{min}$. This response indicates that the Ge is more prone to the chemical etch at low surfactant concentrations. At the increased CMC levels of the surfactants, however, the dissolution

Table III. Dissolution rate responses of the Ge and SiO_2 wafers as a function of $C_{12}TAB$ and SDS concentration.

$C_{12}TAB$	4 mM (0.25×CMC)	16 mM (1×CMC)	32 mM (2×CMC)
Germanium MRR ($\text{\AA}/\text{min}$)	709	405	338
HDP SiO_2 MRR ($\text{\AA}/\text{min}$)	743	620	463
SDS	2 mM (0.25×CMC)	8 mM (1×CMC)	16 mM (2×CMC)
Germanium MRR ($\text{\AA}/\text{min}$)	616	476	394
HDP SiO_2 MRR ($\text{\AA}/\text{min}$)	557	459	369

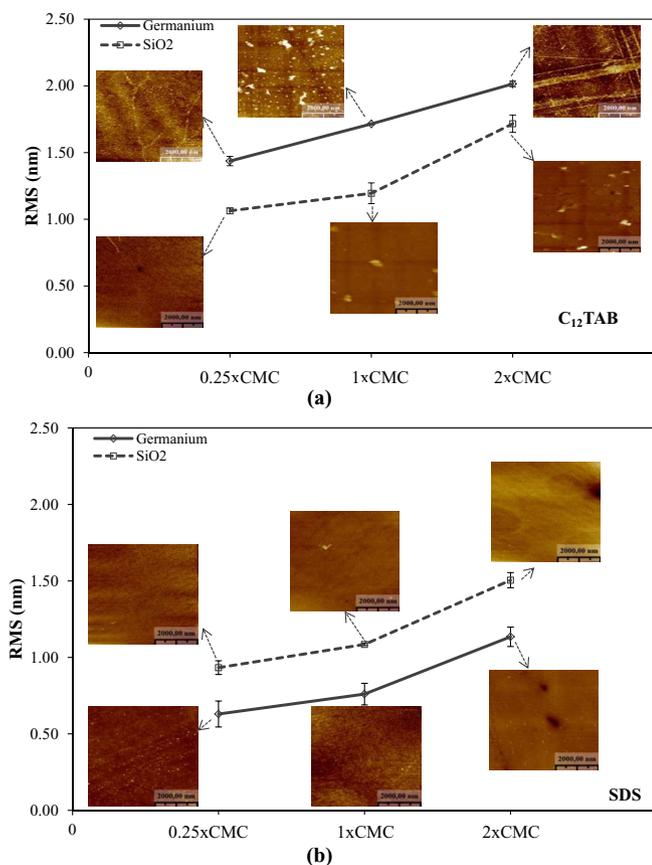


Figure 10. RMS surface roughness measurements and 2-D AFM micrographs on the Ge and silica wafers polished with (a) C₁₂TAB at 4 mM, 16 mM and 32 mM concentrations in the slurry and (b) with SDS at 2 mM, 8 mM and 16 mM concentrations in slurry.

rates decrease continuously, while the MRR responses are higher on Ge pointing to mechanical action of the CMP is playing a role. This is also indicative that the slurry particles can engage mechanically on the Ge surface enhancing its removal rates beyond the chemical dissolution. The level of frictional interactions is known to be changing in the presence of surfactants and oxidizers as a function of the interaction of the surfactant molecules with the available ions in the slurry.^{10,18} The impact of ionic strength on enhancing the Ge removal rate has also been demonstrated by Babu and coworkers in the earlier studies.⁷ Hence, the surfactant interactions as a function of concentration with the hydrogen peroxide needs to be further studied to understand the impact on the surface frictional interactions and material removal response. The MRR and the dissolution rates on silica, on the other hand, decrease in parallel as observed in our earlier work.⁹ The irregular material removal rate results obtained by the C₁₂TAB can be explained by the gel formation at above the CMC concentration of the surfactant which resulted in slurry coagulation. Hence the surface quality needs to be evaluated in parallel to the removal rate responses.

When the surface quality responses of both systems were evaluated, C₁₂TAB was observed to result in a very poor surface quality as it is shown in Figure 10a due to poor stability of the slurry system. Furthermore, the attraction in between the negatively charged surface and positively charged particles due to cationic surfactant addition resulted in sticking of the particles on the surface leading to poor surface roughness measurements. It is shown in detail with the AFM micrographs in Figure 10a that both the surface roughness values and the surface defectivity were not at the acceptable levels in the presence of C₁₂TAB at any concentration. The RMS values were measured to be 1.44, 1.72 and 2.02 on Ge and 1.06, 1.20 and 1.72 on

silica with 0.25 \times , 1 \times and 2 \times CMC levels of C₁₂TAB, respectively. As suggested earlier, it is probable that the C₁₂TAB complexes in the presence of H₂O₂ as can be seen from the agglomeration of the slurries when C₁₂TAB is added. This complex formation can also be the reason for the high selectivity obtained in the presence of C₁₂TAB due to mechanical abrasion, although our initial hypothesis does not suggest this system to provide observed selectivity. Hence, it appears that C₁₂TAB is not the correct choice to obtain the desired selectivity. On the other hand, when SDS was used to modify the CMP slurries, much acceptable surface quality responses were obtained as can be seen in Figure 10b. The RMS values were measured to be 0.63, 0.76 and 1.14 on Ge and 0.93, 1.09 and 1.51 on silica with 0.25 \times , 1 \times and 2 \times CMC levels of SDS, respectively. The increase in the surface roughness and defectivity at the higher concentrations of the surfactants particularly on the Ge surface is indicative of the more mechanical action as discussed through the material removal rate responses. Both the RMS roughness values and the surface defectivity were observed to improve through AFM micrographs when SDS was added as compared to C₁₂TAB. The best results were obtained at 2 mM SDS concentration and pH 6 in the presence of 1 mM oxidizer.

As it is seen in Table II, the selectivity responses were tuned to increase from the baseline value of 3 obtained at pH 6 with 0.1 M H₂O₂ addition to 4.7 with C₁₂TAB and 3.6 with SDS surfactant at quarter CMC dosages. Although it is important to enhance the selectivity of silica removal over the Ge removal for the STI based application of the CMP process,⁸ it has been recently shown that the selectivity requirements can vary for waveguide applications of Ge films with less silica removal required.¹⁹ Hence it is important to be able to control the selectivity response of the Ge/silica system depending on the selected application.¹ Here we have shown that the selectivity of the silica/Ge system can be tuned from 1:1 (2 \times CMC) to 3.6:1 (0.25 \times CMC) by addition of SDS surfactant without compromising the surface quality.

Summary

Selectivity of the Ge/SiO₂ systems can be controlled by using surfactant mediation in the CMP slurries. In this study both cationic and anionic surfactants were evaluated for selectivity performances at 0.25 \times CMC, 1 \times CMC and 2 \times CMC concentrations at optimized slurry pH 6 and 0.1 M oxidizer concentration. Although both surfactants were able to provide enhanced selectivity responses at quarter CMC concentration, the cationic C₁₂TAB was observed to degrade surface quality due to destabilization of the slurry particles. On the other hand, good defectivity control with a sufficient material removal rate response was obtained by using SDS surfactant at the quarter CMC concentration. In summary, it was shown that use of 2 mM SDS at pH 6 and 0.1 M oxidizer concentration could relatively lower Ge CMP material removal rates as compared to oxide removal rates. The systematic approach followed in this paper by measuring the surface and slurry ζ -potentials and comparing the removal rate responses of the different surfaces can be used for development of controlled selectivity systems for other CMP applications where the selectivity is critical to produce defect free interfaces.

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