The chemical mechanical planarization (CMP) removal rate (RR) of germanium using potassium periodate as oxidizer with fumed silica based slurries has been investigated. Static etch rate (ER) of germanium was performed as a function of solution temperature, pH and concentration of potassium periodate. Change in the enthalpy (ΔHate) and entropy (ΔSate) of activation for the Ge in the proposed oxidizer was found to be 11.029 kJ/mol and −271.06 J/mol.K, respectively. The values suggest that the dissolution of germanium in the proposed oxidizer is endothermic in nature and the etching is controlled by activation complex. The effect of slurry pH, KIO4 concentration, turnover speed and down pressure on Ge RR were studied. ER and RR of Ge were found to increase with pH. In the absence of oxidizer, polishing of germanium with 3 wt% fumed silica showed almost zero removal. With the addition of 1 wt% KIO4 + 0.1M KOH to 3 wt% fumed silica slurry, significant increase in the RR of Ge was observed for complete range of pH. Ge is oxidized to form germanium dioxide in the presence of KIO4, which on subsequent oxidation resulted in the formation of soluble species.

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can be converted to film thickness. Ge ER and RR were found by dividing film thickness by polishing time. Ge removal using the proposed slurry was tested for Prestonian behavior, RR (nm/min) = APv where A is Preston coefficient, P is the down pressure and v is the table speed.

**Results and Discussion**

**Etching experiments.**—Effect of KIO₄ concentration on Ge ER.—Etching experiments on Ge were performed by varying KIO₄ concentration ranging between 0.25 wt% to 1.5 wt%. The pH of the solutions with different KIO₄ concentration were adjusted to 11 using HNO₃. It can be depicted from Figure 1 that ER significantly depends on KIO₄ concentration. Ge ER was increased to ∼52 nm/min from ∼6 nm/min with KIO₄ concentration increased to 1 wt% from 0.25 wt%, respectively. This might be due to increased oxidation of Ge surface with IO₄⁻ ions and also due to the formation of soluble dimesoiodate complexes. Further increase beyond 1 wt% of KIO₄ concentration (1.25 wt% and 1.5wt%), as seen in Figure 1, Ge ER was found to be saturated. The observed saturation can be attributed to the limited Ge surface available for oxidation. KIO₄ concentration of 1 wt% with 0.1 M KOH was selected for further study, as there was no remarkable increase in Ge ER above 1 wt% KIO₄ concentration. Ge ER was zero for the pH adjusted distilled water in the absence of KIO₄.

Effect of pH on Ge ER.—At fixed KIO₄ concentration, the effect of solution pH on Ge ER was studied. KIO₄ concentration of 1 wt% was used by adjusting the pH using HNO₃ for this study. An increase in Ge ER with increasing solution pH can be seen in Figure 2. Ge ER was enhanced to ∼52 nm/min from ∼15 nm/min, when pH of the solution was increased to pH 11 from pH 3, respectively. Increase in ER while moving toward alkaline region might be due to the oxidation of Ge surface with IO₄⁻ anions formed from dissociation of KIO₄, as shown in Eq. 1 and with *OH radicals, formed from the dissociation of KOH, as shown in Eq. 2. The observed ER is in line with the reported literature of H₂O₂ system.

\[
\text{KIO}_4 \rightarrow K^+ + IO_4^- \quad [1]
\]

\[
\text{KOH} \rightarrow K^+ + OH^- \quad [2]
\]

Effect of temperature on ER.—The relation between solution temperature and ER was studied in 1 wt% KIO₄ with 0.1 M KOH solution. The pH of etchant solution was maintained at 11. A temperature range 30°C–70°C was selected for dissolution study. The results are shown in Figure 3. The etch rate was found to increase with increase in temperature. At 30°C the ER was ∼58 nm/min, which enhanced to ∼114 nm/min at 70°C. Activation energy for Ge dissolution in potassium periodate solution was calculated using Arrhenius equation, as shown in Eq. 3. Where, A is the Arrhenius pre-exponential factor, \(E_a\) is the activation energy, R is the universal gas constant (8.314 J/mol.K) and T is the absolute temperature (K). Figure 4 shows the semi-logarithm plot of etch rate and 1/T. The activation energy was found to be 13.7 kJ/mol.

\[
\log \left( \frac{\text{ER}}{T} \right) = \log \left( \frac{R}{Nh} \right) + \frac{\Delta S_{\text{act}}}{2.303R} - \frac{\Delta H_{\text{act}}}{2.303RT} \quad [4]
\]

In order to determine the thermodynamic property, the transition state equation was applied to evaluate enthalpy and entropy of activation, as shown in Eq. 4. Where, \(\Delta H_{\text{act}}\) is the enthalpy of activation, \(\Delta S_{\text{act}}\) is the entropy of activation, R is the universal gas constant, h is Planck’s constant (6.626176 × 10⁻³⁴ J-s) and N is Avogadro’s number (6.02252 × 10²³ mol⁻¹). Figure 5 shows the plot of \(\log (ER/T)\) versus 1/T. It can be seen that a straight line is obtained with a slope of \((-\Delta H_{\text{act}}/2.303R)\) and an intercept of \([\log (R/Nh) + (\Delta S_{\text{act}}/2.303R)]\).

**Figure 1.** Effect of KIO₄ concentration on Ge ER at pH 11.

**Figure 2.** Effect of pH on Ge ER using 1 wt% KIO₄ solution.

**Figure 3.** Effect of solution temperature on ER at pH 11.
Effect of KIO₄ concentration on Ge RR.—Figure 7 shows Ge RR at constant pH in presence and absence of 3 wt% fumed silica. For this study the pH was maintained at 11. Ge RR increased with increase in KIO₄ concentration from 0.25 wt% to 1 wt%. Ge RR was found to be zero with 3 wt% fumed silica over the entire range of pH. In the absence of abrasive, the increase in oxidizer concentration from 0.25 wt% to 1 wt% enhances Ge RR from ~61 nm/min to ~160 nm/min. Whereas with addition of 3 wt% fumed silica in polishing slurry, Ge RR was found to increase from ~74 nm/min to ~222 nm/min with KIO₄ concentration increasing from 0.25 wt% to 1 wt%, respectively. The enhanced RR of Ge with increasing KIO₄ concentration might be due to the increased oxidation of Ge with IO₃⁻ and IO₄⁻ anions, as shown in Eqs. 6 and 7. As the concentration of KIO₄ increases, Ge surface oxidizes rapidly to form GeO₂ with subsequent formation of soluble species. With the addition of abrasive, Ge RR is relatively higher, which might be attributed to the combined effect of free abrasive polishing and chemical etching:

\[
2Ge + IO_3^- \rightarrow GeO_2 + I^- \quad [6]
\]

\[
3Ge + 2IO_3^- \rightarrow 3GeO_2 + 2I^- \quad [7]
\]

Effect of pH on Ge RR.—Polishing experiments were performed on Ge in the presence and absence of 3 wt% fumed silica using 1 wt% KIO₄ + 0.1 M KOH solution. Figure 6 illustrates the effect of pH on Ge RR. In the absence of fumed silica, Ge RR enhances from ~37 nm/min to ~160 nm/min when the pH of the slurry was varied from 3 to 11, respectively. Whereas, in the presence of 3 wt% fumed silica with 1 wt% KIO₄ + 0.1 M KOH slurry, Ge removal rate was found to be ~49 nm/min at pH 3 and ~222 nm/min at pH 11. The main cathodic reactions are the reduction of IO₃⁻ to IO₂⁻, as shown in Eq. 5. Increased RR of germanium with pH could be attributed to the availability of OH radicals, IO₃⁻ and IO₄⁻ anions and resulted in the oxidation of Ge surface to form germanium dioxide (GeO₂).

\[
IO_3^- + H_2O + 2e^- \rightarrow IO_2^- + 2OH^- \quad [5]
\]

\[
y = -715.94x - 0.9016 \\
R^2 = 0.9786
\]

Figure 4. Plots of log (ER/T) vs. 1/T for germanium in potassium periodate solution at pH11.

Figure 5. Plots of log (ER/T) vs. 1/T for germanium in potassium periodate solution at pH11.
rate with pressure was distinctly reported for ruthenium/germanium CMP in literature.8,9,28

Effect of table speed on Ge RR.—Figure 10b shows the effect of table speed on Ge RR using 3 wt% fumed silica + 1 wt% KIO4 + 0.1M KOH slurry at pH 11. From Figure 10b, it is clear that as the platen rotational speed is increased from 50 rpm to 250 rpm, Ge RR increases from ∼98 nm/min to ∼321 nm/min. Higher RR is likely due to the rapid formation of GeO2 film on the Ge surface27 and the synergetic effect of oxidation and fast action of abrasive with high table speed.

Surface morphology.—Surface roughness (Ra) of Ge coupons were evaluated at pH 3, pH 7 and pH 11. Before polishing, the surface roughness was found to be 0.72 ± 0.03 μm. Ge coupon polished using 3 wt% fumed silica + 1 wt% KIO4 + 0.1 M KOH slurry at pH 3 showed no significant change in surface roughness. While the germanium coupon polished using the proposed slurry at pH 7 and pH 11, shown surface roughness of 0.66 ± 0.05 μm and 0.41 ± 0.05 μm, respectively. With increase in the pH value of the slurry, Ge surface roughness was found to be decrease. Ge coupons polished with 3 wt% fumed silica + 1 wt% KIO4 + 0.1M KOH at pH 11, shows a surface roughness reduction of ∼42%.

Removal mechanism.—Fumed silica particles are negatively charged over the entire pH range for all the three slurries i.e., 3 wt%
fumed silica, 3 wt% fumed silica + 0.1 M KOH and 3 wt% fumed silica + 1 wt% KIO4 + 0.1 M KOH. According to the literature,5,6 Ge surface have isoelectric point (IEP) between pH 4 and 4.5 in pH adjusted DI water. At pH 3, Ge surface is positively charged and SiO2 particles are negatively charged leading to electrostatic attraction among them and from pH 5 onwards both Ge surface and SiO2 particles are negatively charged leading to repulsion between them. In alkaline region, Ge polishes at higher rate with higher concentration silica based abrasives, where electrostatic repulsion exists between the SiO2 particles and Ge surface.2 Apart from electrostatic interactions, there might be some other reason behind for the higher material removal in the alkaline region.

The increase in material removal with abrasive concentration in the solid-solid contact mode of CMP was reported by Luo24 with a qualitative explanation about active and inactiv abrasive. The material removal increases with more number of active abrasive between the wafer and pad surface, which in turn increases the total contact area among them, till saturation occurs. Ge polished with 3 wt% fumed silica has larger effective diameter, which is due to its presence in agglomerated form contributing to less total surface area. With the addition of 0.1 M KOH, which acts as dispersing agent, the abrasive particles are dispersed with pH, providing more total surface area for interaction. Potassium periodate works as a stabilizer and refrains particles to agglomerate. The interaction between agglomerated / dispersed fumed silica particles and Ge surface, which in turn affects the total contact between the particles and the Ge surface is schematically shown in Figure 11.

Potassium periodate dissociates to form potassium (K+) cation and periodate (IO₄⁻) anion, as shown in Eq. 1. The main cathodic reactions for polishing Ge in KIO₄ solution is the reduction of IO₄⁻ to IO₃⁻ anions,11–14 as shown in Eq. 5. The IO₃⁻ and IO₄⁻ anions oxidizes Ge to form germanium dioxide, according to Eqs. 6 and 7. Literature suggest that the GeO₂ undergoes hydration in the aqueous environment and form germanium hydroxide complex, GeO(OH)₄ and GeO₂(OH)₂−.28 However, the formation of those species strongly depends on the pH value. It can be explained that in the acidic region (pH < 8), the reaction proceeds as shown in Eq. 8 to form of germanic acid, Ge(OH)₄, which is not easily soluble in water resulting in lesser RR. While in the weak alkaline pH range between 8 and 11, the concentration of °OH radicals increases, which enhances the oxidation of germanium and hydration of GeO₂ to form a more soluble dissolution product GeO(OH)₃− as shown in Eq. 9. In the highly alkaline region (pH > 11), the most soluble species, GeO₂(OH)₂− is prevalent in aqueous solution as shown in Eq. 10.5,6

\[
\text{pH} < 8 : \text{GeO}_2 + 2\text{H}_2\text{O} \Leftrightarrow \text{Ge(OH)}_4(aq) \quad [8]
\]

\[
8 < \text{pH} < 11 : \text{GeO}_2 + 2\text{H}_2\text{O} \Leftrightarrow \text{Ge(OH)}_3(aq) + \text{H}^+ \quad [9]
\]

\[
\text{pH} > 11 : \text{GeO}_2 + 2\text{H}_2\text{O} \Leftrightarrow \text{GeO}_2(\text{OH})_2(aq) + 2\text{H}^+ \quad [10]
\]

Conclusions

CMP slurry for polishing Ge disk using 3 wt% fumed silica + 1 wt% KIO4 with 0.1 M KOH was proposed. With increase in temperature ER was found to increase, the activation energy was found to be 13.7 kJ/mol. The enthalpy and entropy of activation are 11.029 kJ/mol and −271.06 J/mol.K, respectively, which suggest that the dissolution of germanium is endothermic process and the dissolution is controlled by means of activation complex. For the same potassium periodate concentration and pH, there was an appreciable increase in the Ge MRR over Ge ER, due to the synergetic effect of free abrasive polishing and chemical etching. The effective diameter of fumed silica abrasive is larger for 3 wt% fumed silica slurry than 3 wt% fumed silica with 0.1 M KOH and 3 wt% fumed silica + 1 wt% KIO4 + 0.1 M KOH slurry for complete range of pH. At pH 11, maximum RR of ~222 nm/min was obtained with 3 wt% fumed silica + 1 wt% KIO4 + 0.1 M KOH slurry. The higher removal in alkaline region could be due to the presence of °OH radicals with increasing pH and also due to increased oxidation of Ge with IO₃⁻ and IO₄⁻ anions. Moreover, with increase in the pH, agglomerated particles gets dispersed, leading to result more contact between Ge coupon and SiO2 particles. Subsequently, Ge oxidizes to form germanium dioxide followed by formation of rapidly soluble Ge hydroxide species. Surface roughness was found to be reduced by ~42% at pH 11. Ge removal with potassium periodate follows non-Prestonian behavior.

Figure 9. Effective diameter as a function pH.

Figure 10. Effect of (a) pressure; (b) table speed on Ge RR using 3 wt% fumed silica with 1 wt% KIO4 at pH 11.
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Figure 11. Interaction between agglomerated and dispersed fumed silica particles in presence and absence of KIO4 for Ge removal.