

**Potassium persulphate based silica slurry for germanium chemical mechanical planarization**Apeksha Gupta<sup>a</sup>, R. Manivannan<sup>\*b</sup> and S. N. Victoria<sup>b</sup><sup>a</sup>Department of Chemical Engineering, Indian Institute of Technology, Guwahati-781 039, Assam, India<sup>b</sup>Department of Chemical Engineering, National Institute of Technology Raipur, Raipur-492 010, Chhattisgarh, India

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This study is based on germanium (Ge) chemical mechanical planarization (CMP) by potassium persulphate (KPS) as oxidizer in fumed silica slurry. All experiments were performed at room temperature to acquire Ge etch rate and removal rate. The effect of pH, tablespeed, downpressure and potassium persulphate concentration on germanium removal rate was studied. Higher etch rate and removal rate were obtained in alkaline pH attributable to higher oxidation of germanium surface followed by fast dissolution of germanium hydroxide complexes. The system followed non-Prestonian behavior. A probable reaction mechanism for germanium removal in potassium persulphate based silica slurry is proposed.

Keywords: Germanium, chemical mechanical planarization, potassium persulphate.

**Introduction**

Silicon (Si) ruled the semiconductor industry since decades. Si complementary metal oxide semiconductor (CMOS) device scaling can be achieved satisfactorily till 45 nm, going below 45 nm with Si does not provide appreciable performance to survive with the recent miniaturized and fast running devices<sup>1</sup>. For present and future scaled down devices Ge is a viable candidate with attractive physical properties over Si, particularly its band gap and hole mobility. For sub-22 nm devices, Ge is a viable candidate with hole and electron mobility of 1900 cm<sup>2</sup>/Vs and 3900 cm<sup>2</sup>/Vs<sup>2</sup>. Ge has lower band gap of 0.66 V as that of Si<sup>3</sup>.

Ge is used as channel material in p-type metal oxide semiconductor (PMOS) devices. During manufacturing of integrated circuits, CMP is the most widely used process to remove extra deposited material. It is the only process that provides local and global planarization<sup>4</sup>. Hydrick *et al.*<sup>5</sup> investigated removal rate (RR) selectivity between Ge and SiO<sub>2</sub>. Ge was polished with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ammonium hydroxide (NH<sub>4</sub>OH) and bleach. With H<sub>2</sub>O<sub>2</sub> and silica system, the Ge and oxide polishing rate was reported as ~400 nm/min and ~100 nm/min, whereas with NH<sub>4</sub>OH, very less material removal was reported. Highest RR was ob-

served with bleach and SiO<sub>2</sub> system, however, high level of metal contaminants and dishing was observed after polishing. Ong *et al.*<sup>6</sup> discussed the integration approach for high mobility channel materials. The selectivity ratio between Ge and silicon dioxide (SiO<sub>2</sub>) was about 3.5:1 after polishing with W-CMP slurry and 0.17 wt% H<sub>2</sub>O<sub>2</sub>. Matovu *et al.*<sup>7</sup> studied Ge polishing by using surfactants and electrolytes. With 0.1 mM concentration of cetyltrimethyl ammonium bromide (CTAB) surfactant highest Ge RR of ~450 nm/min was reported at pH 8. Peddeti *et al.*<sup>8</sup> investigated the significance of pH on Ge RR using H<sub>2</sub>O<sub>2</sub> based colloidal silica slurry. At pH 12, maximum Ge removal rate of ~600 nm/min was reported, which was significantly higher than the removal obtained at acidic and neutral region, ~80 nm/min. Kawamoto *et al.*<sup>9</sup> proposed the significance of pH modulator with abrasive and oxidizer in slurry for higher Ge selectivity and reduced the surface roughness. Three different pH modulators were potassium hydroxide (KOH), triethanolamine (TEA) and N-methylethanolamine (NMEA). Reduction from 1.5 nm to 0.3 nm, 0.5 and 0.3 was reported by using KOH, TEA and NMEA as pH modulators in 3 wt% silica slurry (SCM-070B) and H<sub>2</sub>O<sub>2</sub> slurry (1 mL/L) at pH 10.

For Ge CMP most of the reported work is on H<sub>2</sub>O<sub>2</sub> with silica slurries and its mechanism is extensively studied. Poli-

shing of copper and silicon dioxide using potassium persulfate is notable<sup>10,11</sup>. This work is based on study of potassium persulfate as oxidizer in fumed silica slurry for polishing germanium.

### Experimental

Germanium disk was acquired from Rare World Metals Mint, Cincinnati, USA having 99.999% purity with 1"×0.5" dimension. Fumed silica abrasive particle was purchased from Cabot India (CAB-O-SILs M-5). Suba IV polishing pad was procured from Eminess Technologies, Arizona, USA. Potassium persulfate, potassium hydroxide (KOH) and nitric acid (HNO<sub>3</sub>) of 69% were purchased from Merck Specialities Private Limited, Mumbai, India. For performing all the experiments distilled water was used. Weight loss of Ge disk was investigated by gravimetric analysis using an analytical balance (Sartorius). To modify the pH of solution/slurry KOH or HNO<sub>3</sub> was used.

Ge etch rate (ER) was determined to study the chemical reactivity of Ge with KPS. Ge disk was immersed in 100 ml etchant solution for 3 min followed by distilled water rinse and air drying. Weight loss, density and exposed area of Ge disk were considered to determine etch rate. Average ER was reported after conducting three experimental runs along with standard deviation.

Bench top polisher (StruersLaboPol-5/LaboForce-3) was used to perform CMP experiments. The formulated slurry was transported to bench top polisher machine by using peristaltic pump having steady flow rate of 100 ml/min. Abrasive particles (fumed silica) have tendency to settle down. Magnetic stirrer was used to keep formulated slurry in suspension. The conditioning of polishing pad was performed by using 180 grit size emery paper after each polishing run. Tablespeed of 100 rpm and a downpressure of 1.974 N/cm<sup>2</sup> were used for performing CMP experiments unless and otherwise mentioned. The removal rate was calculated based on weight loss of Ge disk after CMP polishing runs with formulated slurry. The influence of pressure and velocity on Ge removal rate is studied by using Preston's equation as shown in eq. (1)<sup>12</sup>,

$$\text{MRR} = kPV \quad (1)$$

where,  $k$  is Preston's coefficient and it depends on the chemical and mechanical aspects of the polishing process,  $P$  is

pressure and  $V$  is rotational speed of platen. The system which obeys Preston's equation is considered to have Prestonian behavior.

### Results and discussion

#### *Influence of KPS concentration on ER:*

The influence of KPS concentration on etch rate is shown Fig. 1. Before adding KPS, ER for pH adjusted distilled water for entire range was zero. Fig. 1 shows that ER increases with increase in KPS concentration. At 0.5 wt% of KPS, ER is negligible. Increase in KPS concentration increased ER from ~3 nm/min to ~17 nm/min at 3 wt% KPS due to the oxidation of Ge surface. Increase of KPS concentration beyond 3 wt% showed saturation in ER due to limited availability of Ge surface for oxidation. Thus, 3 wt% of KPS was selected for further study.

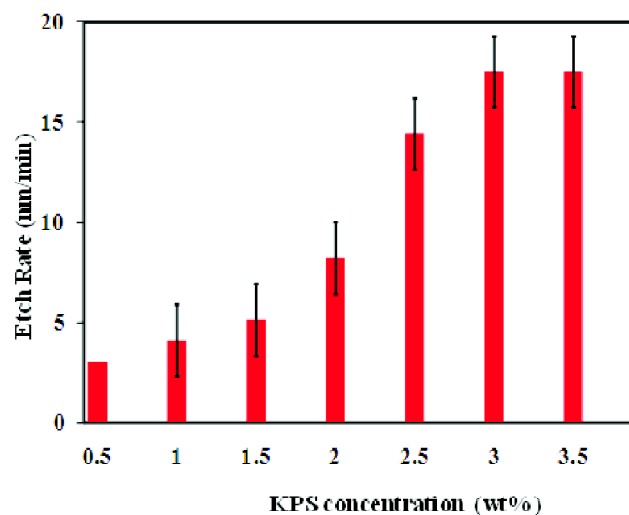


Fig. 1. Influence of KPS concentration on ER at pH 11.

#### *Influence of pH on ER:*

Ge etching experiments were performed by varying pH of solution using 3 wt% KPS concentration, shown in Fig. 2. As the solution pH move towards alkaline side, Ge ER increases. Above pH 8, Ge ER was found to be higher. ER in acidic region (at pH 3) was found to be ~8 nm/min, which increased to ~17 nm/min at pH 11. Germanium oxidizes more due to the oxygen and thus shows higher ER above pH 8.

#### *Influence of temperature on ER:*

Fig. 3 shows influence of KPS solution (3 wt%) tempera-

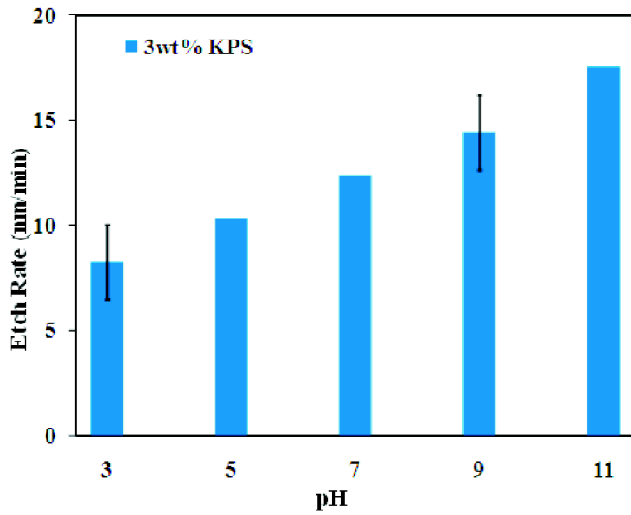


Fig. 2. Influence of pH on ER at 3 wt% KPS.

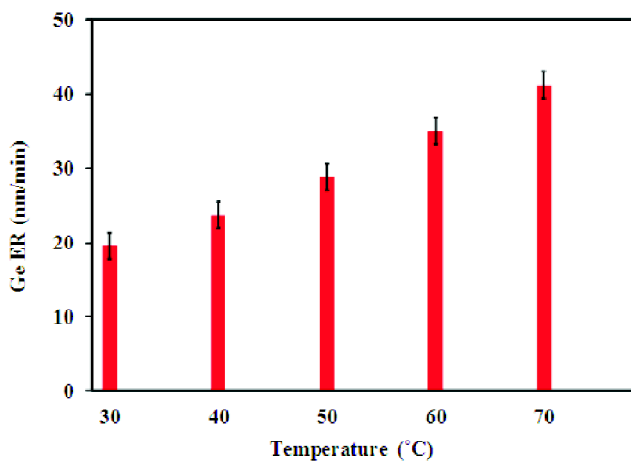


Fig. 3. Influence of temperature on ER at pH 11.

ture on ER at pH 11. The temperature range selected for study was 30–70°C. It was observed that ER increased with increase in solution temperature. As the solution temperature increases from 30°C to 70°C, ER increased from ~19 nm/min to ~41 nm/min. Arrhenius equation was used to estimate activation energy. The Arrhenius equation is shown in eq. (2). Where,  $R$  is the universal gas constant with value 8.314 kJ/K.mol,  $A$  stands for Arrhenius pre-exponential factor,  $E_a$  represents activation energy, and  $T$  is the absolute temperature (K)<sup>13</sup>. Fig. 4 illustrates the semi-logarithmic graph plotted against ER versus  $1/T$ . From the linear fit of the graph, the activation energy was calculated to be 16.24 kJ/ mol.

The thermodynamic property was determined by transi-

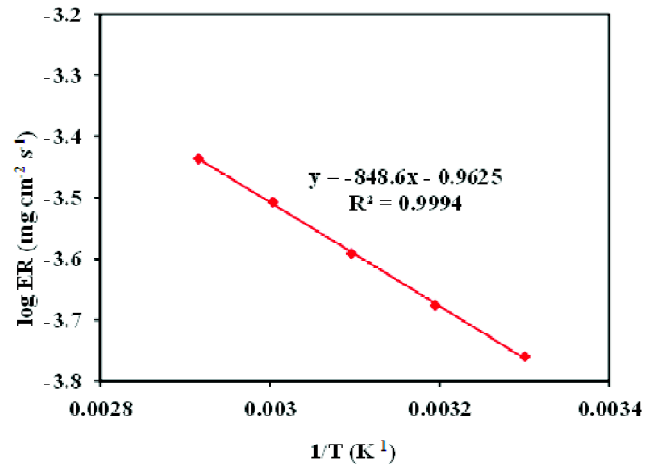


Fig. 4. Depiction of Arrhenius equation for polishing Ge in KPS solution at pH 11.

tion state equation, as represented in eq. (3). Where,  $\Delta H_{act}$  stands for the enthalpy of activation,  $\Delta S_{act}$  stands for entropy of activation,  $N$  stands for Avogadro's number i.e.  $6.02252 \times 10^{23} \text{ mol}^{-1}$ ,  $h$  stands for Planck's constant i.e.  $6.626176 \times 10^{-34} \text{ J}\cdot\text{s}$  and  $R$  stands for universal gas constant. Fig. 5 illustrates plot of  $\log(ER/T)$  and  $1/T$ .  $\Delta S_{act}$  and  $\Delta H_{act}$  were found from intercept  $[\log(R/Nh) + (\Delta S_{act}/2.303R)]$  and slope  $(-\Delta H_{act}/2.303R)$  of a linear fit. The values of  $\Delta H_{act}$  and  $\Delta S_{act}$  were evaluated to be 13.569 kJ/mol and  $-272.17 \text{ J/mol}\cdot\text{K}$ . The positive value of  $\Delta H_{act}$  specify that Ge dissolution in KPS solution is an endothermic process. The negative value of entropy of activation ( $\Delta S_{act}$ ) specify that the

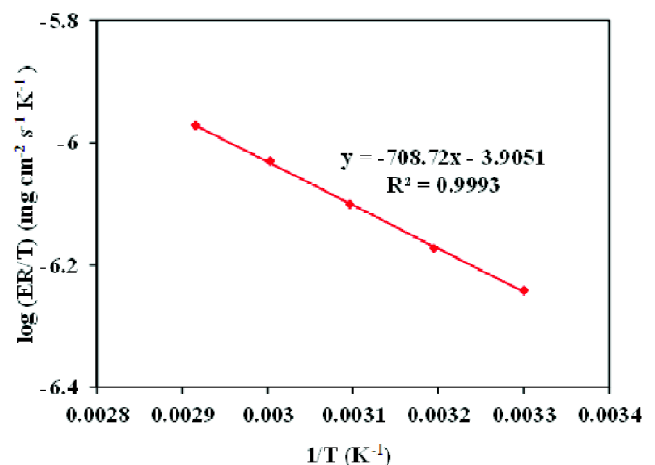


Fig. 5. Depiction of transition state equation for polishing Ge in KPS solution at pH 11.

dissolution mechanism of germanium in KPS solution is achieved through activation complex<sup>13</sup>.

$$\log(ER) = A - \frac{E_a}{2.303RT} \quad (2)$$

$$\log\left(\frac{ER}{T}\right) = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S_{act}}{2.303R} - \frac{\Delta H_{act}}{2.303RT} \quad (3)$$

#### Influence of pH on RR:

Fig. 6 shows CMP polishing of germanium performed with and without fumed silica in KPS concentration (3 wt%). Increase in slurry pH showed increase in removal rate. Ge RR of ~24 nm/min was observed at pH 3 with 3 wt% of KPS, which increased to ~111 nm/min at pH 11. After adding up 3 wt% fumed silica to 3 wt% of KPS solution, RR showed an increase for entire pH range. At pH 3 Ge removal of ~37 nm/min increased to ~136 nm/min at pH 11. Higher removal observed after adding up 3 wt% fumed silica is because of dual action of chemical and mechanical polishing. Oxygen needed for Ge surface to get oxidized is obtained from the dissociation of KPS and peroxydisulphate ( $S_2O_8^{2-}$ ) anion as shown in eqs. (4) and (5). Germanium surface gets oxidized with oxygen to produce germanium dioxide ( $GeO_2$ ). With pH the solubility of germanium hydroxide species shows discrepancy<sup>8</sup>. Maximum germanium removal rate obtained in alkaline region is attributed to higher oxidation of germanium surface with oxygen along with consequent hydrolysis to form

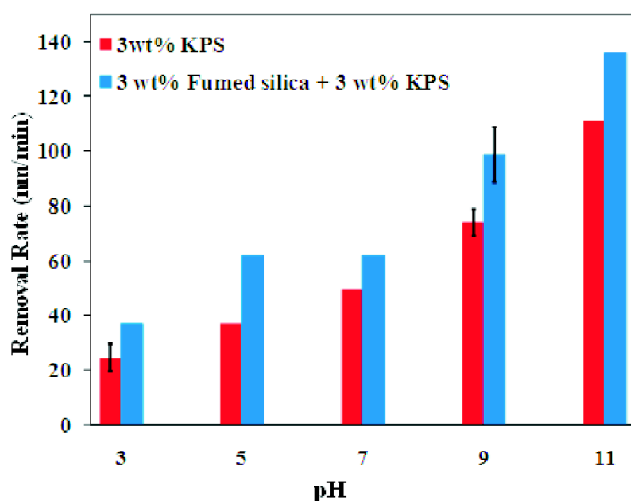


Fig. 6. Influence of pH on Ge RR in the presence and absence of fumed silica in KPS (3 wt%).

easily soluble germanium hydroxide complexes  $GeO(OH)_3^-$  and  $GeO_2(OH)_2^{2-}$ .

#### Influence of downpressure on Ge RR:

To study the influence of downpressure, polishing experiments were performed at pH 11 using same concentration of fumed silica and KPS (3 wt% of slurry). Pressure increase from 1.974 N/cm<sup>2</sup> to 7.898 N/cm<sup>2</sup> showed increase in Ge RR, from ~136 nm/min to ~234 nm/min. The results are illustrated in Fig. 7. As the downpressure is increased on Ge surface the contact between Ge surface and polishing pad increases<sup>14</sup>. This results in increasing RR with increase in downpressure. It can be seen that KPS system in fumed silica slurry for polishing Ge shows non-Prestonian behaviour as it deviates from Preston's equation. The similar trend was reported for polishing ruthenium/germanium in literature<sup>15,16</sup>.

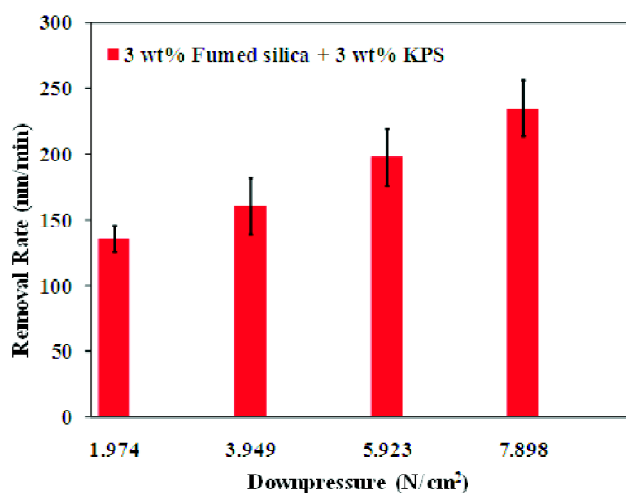


Fig. 7. Influence of downpressure on Ge RR using fumed silica and KPS (3 wt%) at pH 11.

#### Influence of tablespeed on Ge RR:

For polishing experiments using 3 wt% fumed silica and 3 wt% KPS was studied at pH 11. The results are illustrated in Fig. 8. With 50 rpm of platen rotational speed Ge RR was ~74 nm/min. Increasing number of rotations per minute enhanced removal rate. At 250 rpm removal rate reached to ~247 nm/min. The enhanced RR with increasing tablespeed is attributed to quick formation and removal of  $GeO_2$  film from Ge surface<sup>15</sup>. The similar trend was reported in literature<sup>15,17</sup>.

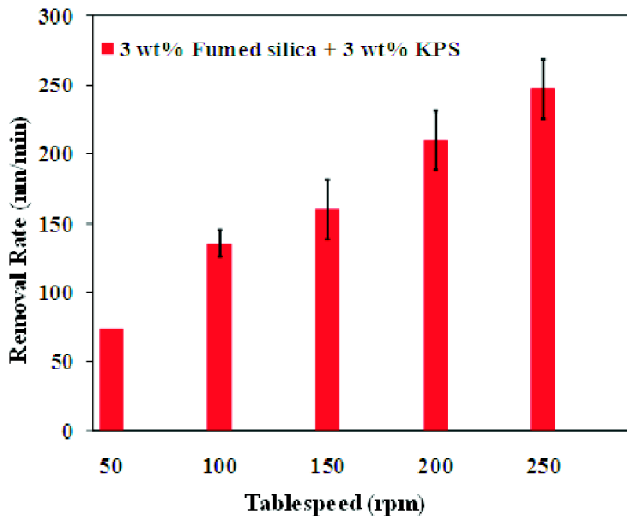


Fig. 8. Influence of tablespeed on Ge RR using fumed silica and KPS (3 wt%) at pH 11.

*Influence of KPS concentration on RR:*

Polishing experiments were performed with varying concentration of KPS at pH 11 with and without fumed silica. With rise in KPS concentration from 0.5 wt% to 3 wt% of the solution, RR of Ge enhanced from 12 nm/min to 111 nm/min. After adding fumed silica (3 wt%) in KPS solution, RR raised to 136 nm/min from 24 nm/min. The results are illustrated in Fig. 9. Higher removal rate observed with increase in KPS concentration is probably because of the enhanced oxida-

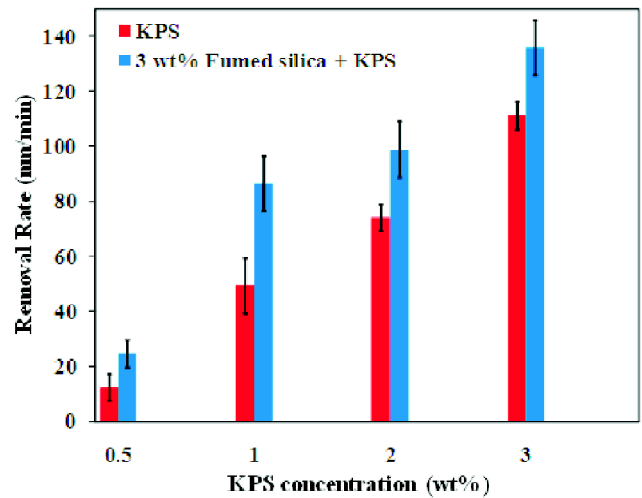


Fig. 9. Influence of KPS concentration on Ge RR in the presence and absence of fumed silica (3 wt%).

tion of Ge. As the KPS concentration increases more oxygen is generated as shown in eq. (5), which further oxidizes Ge surface. Also, addition of abrasive enhances RR due the added mechanical action to chemical action.

*Proposed removal mechanism:*

KPS dissociates to form potassium ( $K^+$ ) cation and peroxydisulphate anion<sup>18</sup>. The dissociation reaction is shown in eq. (4). Peroxydisulphate is supposed to be very strong oxidizer<sup>19</sup>. In aqueous solution, above pH > 0.3, peroxy-

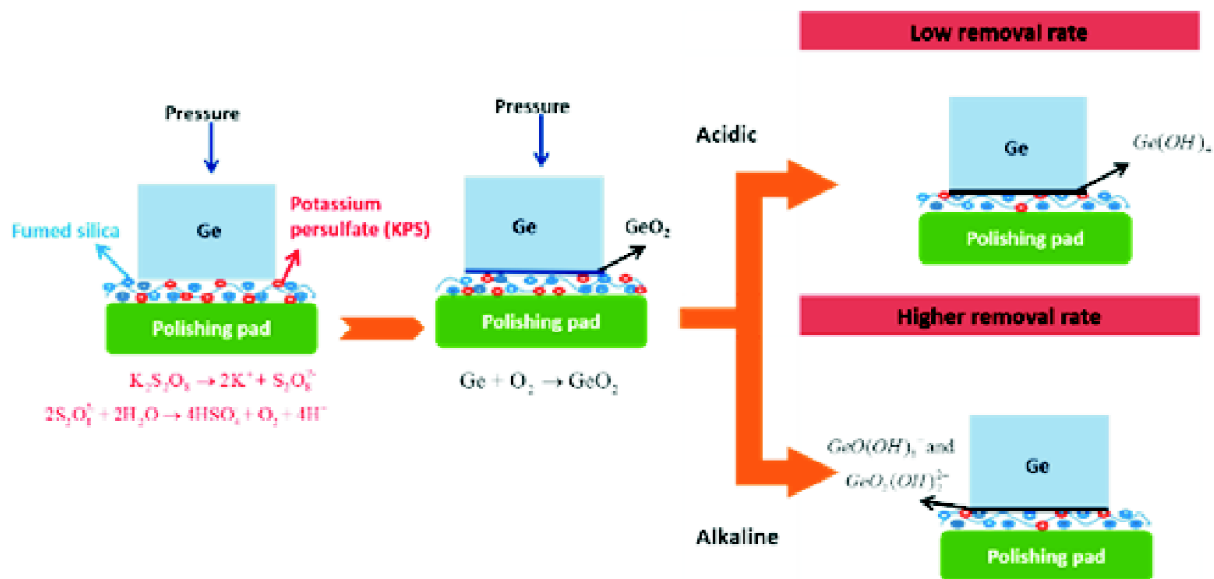
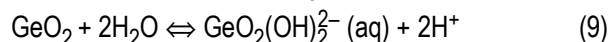
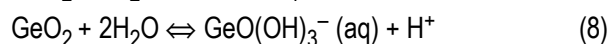
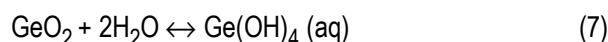
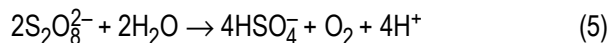


Fig. 10. Germanium removal mechanism in fumed silica slurry containing KPS<sup>16</sup>.

disulphate undergoes thermal decomposition reaction as shown in eq. (5)<sup>20</sup>. Ge needs oxidizer to form germanium dioxide, which dissolves by forming its soluble oxides in water<sup>2</sup>. The formed oxygen reacts with Ge surface, as shown in eq. (6) to form germanium dioxide. Pourbaix diagram of Ge is reported in literature<sup>21</sup>. Germanic acid, Ge(OH)<sub>4</sub>, is prevalent in acidic region (pH < 8) which exhibit least solubility in water. However, in alkaline region, germanium hydroxide complexes, GeO(OH)<sub>3</sub><sup>-</sup> and GeO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup>, are dominant, which are the most soluble species<sup>7,8,21</sup>.

In the present study, Ge surface is oxidized from the released oxygen. Lower Ge RR in acidic region is attributed to limited oxidation of germanium surface to form germanic acid, shown in eq. (7), which have lowest solubility. With increase in pH, Ge surface is oxidized more from the released oxygen (eq. (5)) to form the easily soluble species of germanium hydroxide, GeO(OH)<sub>3</sub><sup>-</sup> and GeO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup>, as shown in eqs. (8)- (9). Hence, Ge RR is appreciably higher in alkaline region. Schematic representation of germanium removal mechanism in fumed silica slurry containing KPS at different pH is shown in Fig. 10.



## Conclusions

KPS was used as an oxidizer for Ge CMP in fumed silica slurry. The concentration of oxidizer and abrasive was fixed to 3 wt% of the slurry. Etch rate was determined from etching experiments to study the significance of chemical action. Maximum ER of ~17 nm/min was obtained at pH 11. CMP runs were performed to study the combined effect of chemical and mechanical action on Ge RR. At pH 11, higher Ge removal rate of ~136 nm/min was observed. The higher RR in alkaline region is due the fact that Ge surface oxidizes more to form GeO<sub>2</sub> with subsequent hydrolysis to form easily soluble germanium hydroxides complexes, GeO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup> and GeO(OH)<sub>3</sub><sup>-</sup>. The KPS system in fumed silica slurry followed non-Prestonian behavior.

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