Influence of Temperature on Thermodynamic Property of Germanium in Hydrogen Peroxide Solutions

Apeksha Gupta, Atul Shukla, S Noyel Victoria, R Manivannan[*]

Department of Chemical Engineering, National Institute of Technology Raipur (C.G), India.

[*] Corresponding author: R Manivannan Email: rmani.che@nitrr.ac.in

ABSTRACT

Germanium (Ge) is considered as a promising candidate to replace Si in the future metal oxide semiconductor field effect transistor (MOSFET) devices, due to its higher electron and hole mobility. Excess Ge, after deposition in the device manufacturing, needs to be removed during chemical mechanical planarization process using slurry containing the oxidizing agent. Hydrogen peroxide (H_2O_2) is widely used oxidizer to remove the excess germanium. However, the thermodynamic behaviour of germanium in hydrogen peroxide system was not studied. In this study, the germanium etch rate (ER) experiments were performed at different temperature in the presence of 0.1 wt% hydrogen peroxide at natural pH. The duration of etch rate experiment was maintained for a min. An increase in etch rate was found with increase in temperature and the thermodynamic properties of the system were investigated. The activation energy for germanium dissolution in hydrogen peroxide system is calculated by using Arrhenius equation and is found to 33.31 kJ/ mol. The enthalpy and entropy of activation for germanium dissolution in hydrogen peroxide system are evaluated from the plot of log (ER/T) versus 1/T. Thermodynamic property of germanium in the proposed system is reported.

Keywords: Germanium, Etch rate, Activation energy, Hydrogen peroxide.
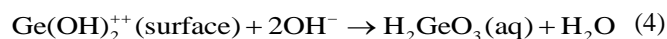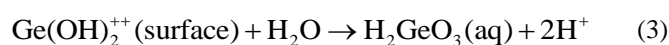
1 INTRODUCTION

Continuous decrease in feature size of integrated circuit (IC) in microelectronics industry generated an intense need for high mobility channel materials. One of the active components of IC is transistor. Silicon is conventionally used for transistor manufacturing. Germanium and III-V compound semiconductor is an alternative to replace silicon as channel material in transistor for next generation devices [1]. To achieve the device shrinkage and faster performance, there is an increased focus towards Ge as channel material for sub-22 nm devices with electron and hole mobility of 3900 cm^2/Vs and 1900 cm^2/Vs as compared to silicon [2]. Ge is considered as a promising candidate for integrating p-type metal oxide semiconductor (PMOS) channel for future metal oxide semiconductor field effect transistor (MOSFET) devices [3].

Device integration needs chemical mechanical planarization (CMP), which is a crucial step for removing the excess material and leave a plane surface [4]. Dissolution study is conducted to investigate the effect of chemical action on germanium and determine the Ge etch rate. Primal et al. [5] studied the dissolution of germanium in hydrogen peroxide (H_2O_2) solution. The effect of pH on the etching rate of germanium using 3 wt% aqueous hydrogen peroxide showed a minimum dissolution rate (DR) of 0.021 μm/min at pH 4. Kagawa et al. [6] reported that H_3PO_4-H_2O_2-H_2O solution could be used as a reliable etchant for Ge. They reported maximum etching rate at 4:6 ratio of H_3PO_4 to H_2O_2. Huygens et al. [7] reported the dependence of germanium ER in hydrogen peroxide solutions at different values of pH. They put forward a mechanism for the etching reaction, involving adsorption of peroxide, followed by local hole injection by adsorbed peroxide, which caused the formation of oxidized surface species that ultimately desorbs

and dissolves. It was noticed that the etch rate in alkaline was higher than that in neutral and acidic H_2O_2 solutions. A two-step mechanism for Ge dissolution in H_2O_2 solution was proposed by Cerniglia et al. [8]. The proposed mechanism was that H_2O_2 dissociates as shown in Eq.1.

$$2H_2O_2 \rightarrow H_3O_2^+ + O_2H^- \tag{1}$$

The O_2H^- ions diffuses onto the surface and attaches with the surface atom forming surface complexes. These surface complexes then react as shown in Eq. 2 and 3 to form metagermanate and metagermanic acid.

$$Ge + O_2H^- + H_2O + 2e^+ \rightarrow Ge(OH)_2^{++} + OH^- \tag{2}$$

$$Ge(OH)_2^{++}(surface) + H_2O \rightarrow H_2GeO_3(aq) + 2H^+ \tag{3}$$

$$Ge(OH)_2^{++}(surface) + 2OH^- \rightarrow H_2GeO_3(aq) + H_2O \tag{4}$$

In this work the germanium dissolution rate is studied at different temperatures in the presence of 0.1 wt% hydrogen peroxide at natural pH. Activation energy needed for the dissolution of Ge in H_2O_2 solution is evaluated and other thermodynamic properties are investigated based on the dissolution rate.

2 EXPERIMENTAL

Ge disk with 99.999% purity of 1 in. diameter and 0.5 in. tall, procured from RWMM (Rare World Metals Mint, USA), was used in this work. Oxidizer, hydrogen peroxide was obtained from Merck Specialities Private Limited, India. Dissolution rate experiments were performed by immersion of Ge

coupons in a beaker containing 200 ml of etchant solution to investigate the chemical action of H_2O_2 on etch rate for predetermined time interval of a min. Sample was taken out and subsequently washed with distilled water and air dried. Sample was weighed before and after the immersion using Sartorius analytical balance of 0.0001 g readability. The gravimetric method was used to determine the Ge ER and the reported data were obtained by taking the average of three experiments, each spanning at least a min of immersion period. Water bath used for the temperature study of etch rate experiments, was purchased from Pooja Scientific Instruments, India.

3 RESULTS AND DISCUSSION

3.1. Effect of H_2O_2 concentration on Ge ER:

Etch rate was studied by varying hydrogen peroxide concentration from 0.025 wt% to 0.15 wt%. It can be clearly seen in Fig. 1 that the etch rate greatly depends on the H_2O_2 concentration. Ge ER was found to increase from ~3 nm/min to 12 nm/min when the concentration of H_2O_2 was increased from 0.025 wt% to 0.1 wt%. This might be due to more oxidation of Ge surface with increase in *OH radicals which favour the formation of soluble Ge hydroxide. Saturation in ER was observed above 0.1 wt% H_2O_2 concentrations (Fig.1), which can be attributed to the limited surface available for oxidation. Thus, 0.1 wt% H_2O_2 concentration was selected for further study.
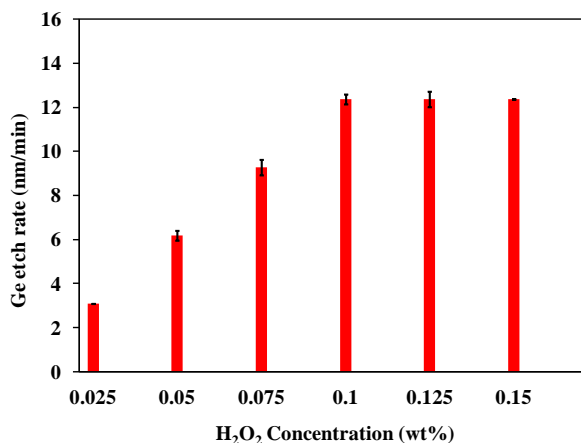

Figure 1: Effect of hydrogen peroxide concentration on ER at natural pH.

3.2. Effect of temperature on Ge ER

The relation between solution temperature and ER was studied in 0.1 wt% H_2O_2 concentration at natural pH (6-7). A temperature range of 30˚C-60˚C was selected for dissolution study. The results are shown in Fig. 2. The etch rate was found to increase with increase in temperature. At 30˚C, the ER was ~18 nm/min, which enhanced to ~64 nm/min at 60˚C. Activation energy for Ge dissolution in H_2O_2 solution was calculated using Arrhenius equation, as shown in Eq. (5). Where, A is the Arrhenius pre-exponential factor, E_a is the activation energy, R is the universal gas constant (8.314 kJ/K.mol) and T is the absolute temperature (K) [9]. Fig. 3 shows the semi-logarithm plot of etch rate and 1/T. The activation energy was found to be 33.31 kJ/ mol.

$$\log(ER) = A - \frac{E_a}{2.303RT} \tag{5}$$

$$\log\left(\frac{ER}{T}\right) = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S_{act}}{2.303R} - \frac{\Delta H_{act}}{2.303RT} \tag{6}$$

To investigate the system thermodynamics, the transition state equation was applied to evaluate enthalpy and entropy of activation, shown in Eq. (6). Where, ΔH_{act} is the enthalpy of activation, ΔS_{act} is the entropy of activation, R is the universal gas constant, h is Planck's constant (6.626×10^{-34} J-s) and N is Avogadro's number (6.02252×10^{23} mol^{-1}). Fig. 4 shows plot of log (ER/T) versus 1/T. It can be seen that a straight line is obtained with a slope of (-ΔH_{act} /2.303R) and an intercept of [log (R/Nh) + (ΔS_{act} /2.303R)]. The calculated values of ΔH_{act} and ΔS_{act} are 30.689 kJ/mol and -215.537 J/mol.K. The calculated value ΔH_{act} is positive, which indicates that the dissolution process of germanium in hydrogen peroxide solution is endothermic in nature. A negative ΔS_{act} value shows that the dissolution of Ge in hydrogen peroxide solution is controlled by activation complex [10].
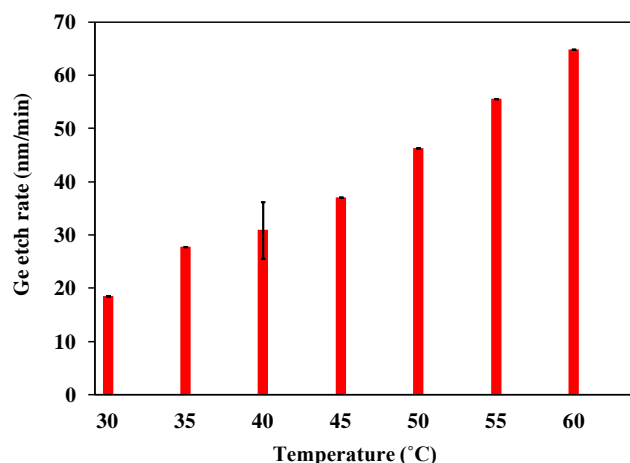

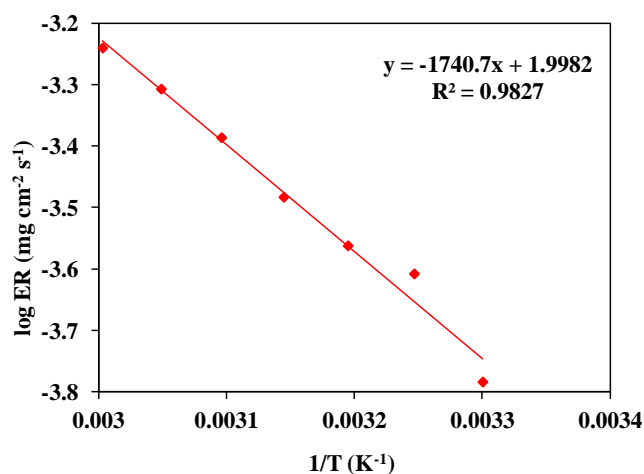Figure 2: Effect of solution temperature on ER at natural pH.

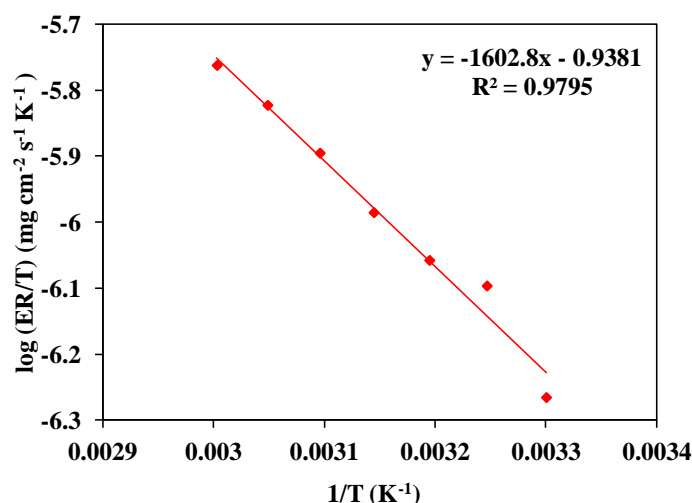Figure 3: Plot of log (ER) versus 1/T for Ge in 0.1 wt% H_2O_2 solution at natural pH.

Figure 4: Plot of log (ER/T) versus 1/T for Ge in 0.1 wt% H_2O_2 solution at natural pH.

4 CONCLUSIONS

Dissolution study of Ge in H_2O_2 solution at natural pH was investigated. Increase in H_2O_2 concentration enhanced etch rate till 0.1 wt% H_2O_2, above that the removal was found to be saturated. Rise in solution temperature showed an increasing in ER with activation energy of 33.31 kJ/ mol. Thermodynamic properties such as enthalpy and entropy of activation was evaluated from transition state equation. The calculated value of ΔH_{act} and ΔS_{act} are 30.689 kJ/mol and -215.537 J/mol.K respectively. A positive value of ΔH_{act} indicates that the dissolution process of germanium in hydrogen peroxide solution is endothermic in nature. A negative ΔS_{act} value shows that the dissolution of Ge in hydrogen peroxide solution is controlled by activation complex.

ACKNOWLEDGEMENTS

REFERENCES

[1] K. J. Kuhn, (2012), "Considerations for ultimate CMOS scaling", *IEEE Trans. Electron Dev.*, 59(7), 1813-1828.

[2] E. Simoen and C. Claeys, (2007), "Germanium-based technologies: from materials to devices", Elsevier, Amsterdam.

[3] S. Peddeti, P. Ong, Leunissen, L. H. A. and S. V. Babu, (2012), "Chemical mechanical planarization of germanium shallow trench isolation structures using silica-based dispersions", *Microelectron. Eng.*, 93, 61-66.

[4] D. Zhao and X. Lu, (2013), "Chemical mechanical polishing: theory and experiment", *Friction*, 1(4), 306-326.

[5] W. Primak and R. Kampwirth, (1967), "Peroxide etching of germanium", *ECS J. Solid State Sci. Technol.,* 114(1), 88-91.

[6] S. Kagawa, T. Mikawa and T. Kaneda, (1982), "Chemical etching of germanium with H_3PO_4-H_2O_2-H_2O solution", *Jpn. J. Appl. Phys*, 21(11), 1616.

[7] I.M. Huygens, W.P. Gomes and K. Strubbe, (2007), "Etching of germanium in hydrogen peroxide solutions", *ECS Trans.*, 6 (2), 375-386.

[8] N. Cerniglia and P. Wang, (1962), "Dissolution of germanium in aqueous hydrogen peroxide solution", *J. Electrochem. Soc.*, 109(6), 508-512.

[9] K. Yadav, J. C. Bisen, S. N. Victoria and R. Manivannan, (2017), "Sodium hypochlorite as an oxidizing agent in silica based ruthenium chemical mechanical planarization slurry", *Microelectron. Eng.*, 180, 96-100.

[10] S. N. Victoria, R. Prasad, and R. Manivannan, (2015), "Psidium guajava leaf extract as green corrosion inhibitor for mild steel in phosphoric acid", *Int. J. Electrochem. Sci.*, 10, 2220-2238.