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An investigation on thermodynamic properties of quartz and borosilicate glass in hydrofluoric acid (HF) medium

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Glass has become a key ingredient in microsystem technology. Etching of quartz and borosilicate glass in hydrofluoric acid is conducted to investigate the material removal for various applications. This is ascribable to their inherent unique properties. In this present study, effect of time, etchant composition and temperature on static etch rates of two different glass coupons were investigated. The results divulge that etch rates tend to increase with time, HF concentration and solution temperature. Further thermodynamic analysis of dissolution process was performed to evaluate the Arrhenius energy, enthalpy and entropy of activation of the glass coupons in HF medium. Borosilicate showed higher activation energy in comparison with quartz. Endothermic nature of dissolution process is confirmed by the positive value of enthalpy. Negative sign of entropy reflects that activation complex is controlling the process of dissolution.

Keywords: Glass, hydrofluoric acid, etching, thermodynamic analysis.

Introduction

A shift towards advanced fabrication techniques in optical and electronic device domain has been observed due to the proliferating trend on miniaturisation concept. Now a days, apart from silicon the most commonly used material in microsystem technology is glass[1]. This is due to their unique innate mechanical and optical properties influenced by quality of the surface[2]. Static etching of glass in hydrofluoric acid (HF) is studied for various applications. Material removal from glass can be obtained by controlled dissolution in etchants based on HF[3].

Silicate glasses are dissolved easily by HF or other HF based solutions. The simplified reaction for dissolution of silicate glass is given by the eq. (1)[4].

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (1)$$

Several applications of etching are extensively investigated, with some effective results in micromachining, micro optics, pre-treatment of silica sand, and sensor applications[5–8]. Etch rate (ER) is a property dependant on the glass type[3]. Independent evaluation is necessary for silicate and multicomponent silicate glasses. Iliescu *et al.* studied the effect of etchant composition and time on ER[1]. Influence of glass composition was examined by Pavelescu *et al*[9]. Spierings worked on multicomponent silicate glasses extensively to identify composition effect[10]. Hirota *et al.* and Kolli *et al.* studied effect of time on ER, finding uses in diverse fields[16,2]. Most etching experiments are based on the effect of etchant concentration and glass composition[3].

Etching experiments were performed to attain a fine understanding on the removal mechanism of silicate glasses. The effects of time, HF concentration and temperature on static etch rates of quartz and borosilicate glasses were studied. So far very few literatures have been reported on thermodynamic study of dissolution process for quartz and borosilicate glasses in HF medium. To evaluate the temperature effect, temperature was varied at a fixed concentration of HF medium. In this present work thermodynamic analysis was carried out to determine activation energy (E_a), enthalpy of activation (ΔH_{act}) and entropy of activation (ΔS_{act}) of glass coupons. This pave way for knowledge on thermodynamic basis of silicate and multicomponent silicate glasses, which is useful in the field of microsystem technology.

Experimental

Materials:

Quartz and borosilicate disks of 1 in diameter and 0.5 in thickness were purchased from Whiteness Signage Solutions, India. Hydrofluoric acid (40% AR) was obtained from Merck Life Science Private Limited, India. The density of quartz and borosilicate glass was taken as 2.65 and 2.23 g cm^{-3} respectively in this work[11,12].

Etching experiments:

Effect of etching time, HF concentration and temperature on static etch rates of different glasses was conducted. Influence of time on etch rate was evaluated by immersing ingots in a fixed concentration of HF for different time periods. To investigate the HF concentration effect, coupons were immersed in HF at various concentrations for 10 min. In pursuance to identify the effect of temperature, ingots immersed at a fixed HF concentration were kept inside a water bath (Thermotech TH-012) at varying temperatures and for a fixed time period of 10 min. Using an analytical balance (Sartorius Model, BSA2245-CW) having readability of 0.0001 g, weight of ingots were measured, pre- and post-immersion. Each time these coupons were washed with distilled water and then dried. Three runs were conducted per case and their mean rates were recorded along with standard deviation. Etch rate was calculated using the weight loss, density, area and immersion time period[13,14].

Results and discussion

Effect of time:

Fig. 1 reveals the influence of time on etch rate. An increase in time resulted in higher rate of etching for both the coupons. This trend observed is consistent with the existing literatures[15,16]. With a dipping time of 2 min, quartz showed a very low etch rate of 2.48 nm/min, which increased to 21.72 nm/min at 10 min. For borosilicate, etch rate varied from 21.38 nm/min to 71.53 nm/min at the same time span. Borosilicate exhibited higher etch rate than the quartz glass for each time. This gives a plausible confirmation that providing more immersion time, more network structure of 'silicate' can be splintered on reaction with HF[3].

Effect of HF concentration:

The effects of HF concentration on static etch rates of quartz and borosilicate glass coupons were studied and obtained results are shown in Fig. 2. Etch rates for both quartz and borosilicate increased with HF concentration, which is in congruence with the reported literature[3]. With increase in the concentration of HF from 0.25 *N* to 1.5 *N*, etch rate for quartz raised from 8.95 nm/min to 33.38 nm/min. pH of the solution was 1.7±0.2. At the same condition, borosilicate followed a similar trend with an increase from 12.96 nm/min to 87.49 nm/min. A linear dependency of etch rate for both on HF concentration was thus observed, while etch rates for borosilicate stood more profound. This can be attributed to reduced silicate content[3]. Multicomponent silicate glasses possess lower silicate content. Thus less such network needs to be broken, which eventually results in higher ER.

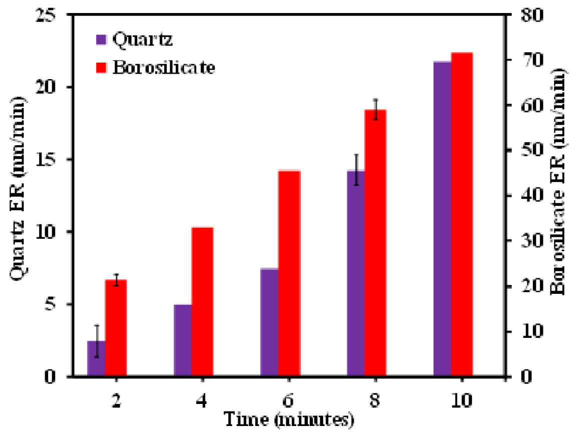

Fig. 1. Effect of time on etch rate of quartz and borosilicate glass in 1.25 *N* HF.

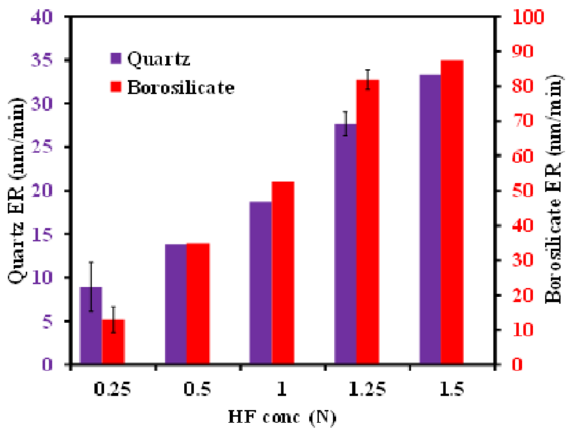

Fig. 2. Effect of HF concentration on etch rate of quartz and borosilicate glass.

Effect of temperature:

Fig. 3(a) and (b) evinces the significance of temperature on static etch rates of quartz and borosilicate coupons at different HF concentrations. As the temperature increases, etch rates also increases for quartz as well as borosilicate. Etch rate increased from 14.27 nm/min to 47.78 nm/min in 1 *N* HF and from 21.1 nm/min to 53.99 nm/min in 1.25 *N* HF for quartz by varying the temperature from 31°C to 51°C. For the same conditions, borosilicate shown a steep rise in etch rate from 47.93 nm/min to 253.70 nm/min in 1 *N* HF. It varied from 74.48 nm/min to 274.35 nm/min in 1.25 *N* HF. But in comparison with concentration effect, higher etch rates were observed on increasing the temperature indicating its significance. This can be ascribed to improved rate of chemical reaction and eventually, faster rate of etching[19].

In pursuance of thermodynamic study, activation energy (E_a) was calculated using Arrhenius equation[17].

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

A semi logarithmic plot of *ER* versus 1/*T* was used to calculate the activation energy and Arrhenius factor as shown in Fig. 4(a) and (b), in which E_a, *T*, *R* and *A* are the activation energy, absolute temperature, universal gas constant and Arrhenius factor respectively. For quartz, activation energy was calculated as 48.53 kJ/mol and 37.43 kJ/mol, while for borosilicate it was found to be 67.03 kJ/mol and 53.08 kJ/mol at 1 and 1.25 *N* HF respectively.

Transition state equation was used to evaluate the en-

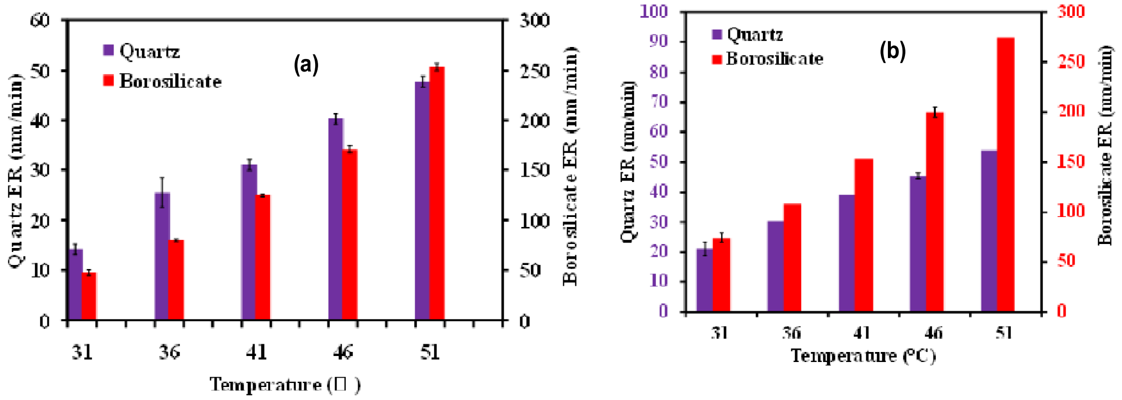

Fig. 3. Effect of temperature on quartz and borosilicate glass in (a) 1 *N* and (b) 1.25 *N* HF.

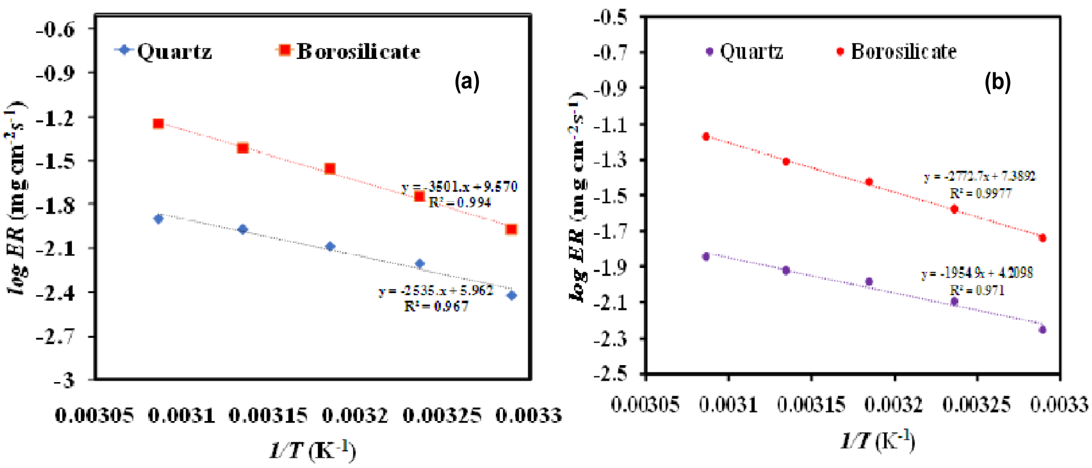

Fig. 4. Arrhenius plot for quartz and borosilicate glass in (a) 1 *N* and (b) 1.25 *N* HF.

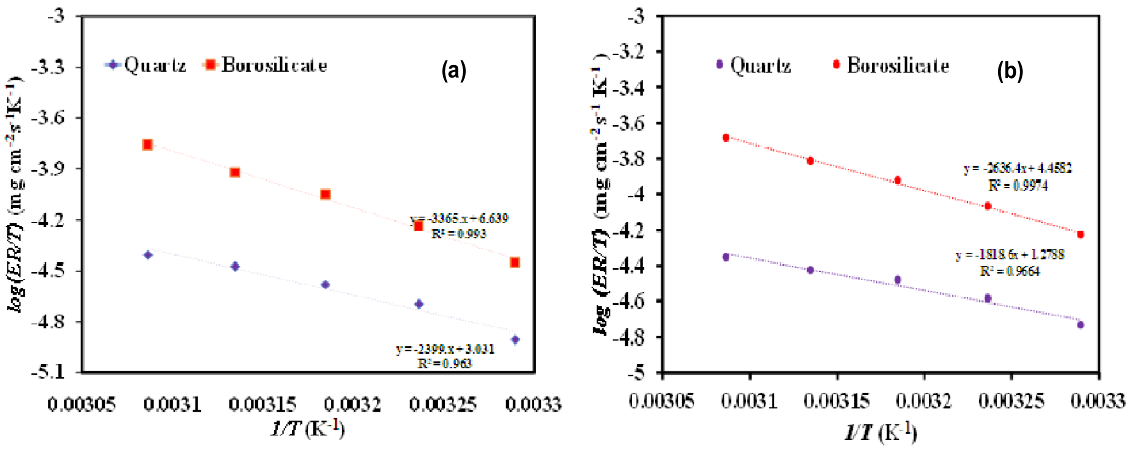

Fig. 5. Plot of log *ER/T* vs 1/*T* for quartz and borosilicate in (a) 1 *N* and (b) 1.25 *N* HF.

Table 1. Activation parameters of quartz and borosilicate in 1 *N* and 1.25 *N* HF

Glass material	HF concentration (N)	E_a (kJ/mol)	ΔH_{act} (kJ/mol)	ΔS_{act} (J/mol.K)
Quartz	1	48.53	45.93	−139.53
	1.25	37.43	34.82	−173.08
Borosilicate	1	67.03	64.43	−70.45
	1.25	53.08	50.47	−112.21

thalpy and the entropy of activation[18].

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

where, N is Avogadro's number (6.02252×10^{23} mol^{-1}), h is Planck's constant (6.626176×10^{-34} Js), R is the universal gas constant (8.314 J/mol. K), ΔS_{act} is the entropy of activation and ΔH_{act} is the enthalpy of activation. Table 1 shows the calculated values of ΔS_{act} and ΔH_{act} from the plot for log (*ER/T*) versus 1/*T* (Fig. 5(a), (b)), which gives straight line having a slope of $-\Delta H_{act}/2.303R$ and an intercept at (log (R/Nh)+($\Delta S_{act}/2.303R$)). Endothermic nature of the process is confirmed by the positive value of enthalpy ΔH_{act}[19]. Negative sign of entropy ΔS_{act} reflects that the activation complex is controlling the dissolution process[20]. A trend for decrease in activation parameters with increase in HF concentration can be observed for both glasses. This is in congruence with reported literature[21,3].

Conclusions

Significance of etching time, etchant concentration and temperature on static etch rate were investigated in this study by performing static etching of quartz and borosilicate coupons in HF medium. Static etch rates increased with time, etchant concentration and temperature. Different etch rates observed for quartz and borosilicate can be ascribed to variation in silicate content. Endothermic nature of the dissolution process is confirmed by the positive value of enthalpy (ΔH_{act}). Negative sign of entropy (ΔS_{act}) reflects that the activation complex is controlling the dissolution process.

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