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The effects of diffusion coefficient on the etching process of sacrificial oxide layers

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Abstract

The etching rate in hydrofluoric acid (HF) of a sacrificial oxide layer decreases during the extended etching process, as indicated by experiments with temperature from 298 to 308 K at different HF concentration. Existing models indicate that the etching solution's concentration at the etching front decreases during extended etching since the diffusion distance of HF from the source of the solution increases, resulting in the decrease of the etching rate. However, it is found that the measured etching rates do not decrease as seriously as predicted by the models. The difference of etching rate between the experiments and the model can reach as high as 30% for extended etching process. A modified model is proposed to explain this phenomenon by considering the diffusion coefficient of HF as a function of concentration in the solution. In the modified model, the decrease of the HF concentration causes the increase of the HF diffusion coefficient, which will partly compensate the decrease of the concentration caused by the long diffusion distance. In addition, the diffusion coefficient as a function of temperature is also included in the modified model. It is found that the modified model matches well the experimental data.

Keywords: Diffusion coefficient; etch rate; sacrificial oxide; Micro-electro-mechanical systems

Variable List

Variable	Units	Description
A_1	[cm/s]	Constant for the first order etching rate coefficient
A_2	[cm^4/(mol·s)]	Constant for the second order etching rate coefficient
C	[mol/l]	HF concentration at etched channel
C_b	[mol/l]	Bulk HF concentration
$C_{b(n)}$	[mol/l]	Bulk concentration of species n
$C_{n(n=1\sim3)}$	[mol/l]	The concentrations to calculate A_1, A_2 and E_a
D	[cm^2/s]	Diffusion coefficient
D_n	[cm^2/s]	Diffusion coefficient of species n
$D_0(T)$	[cm^2/s]	Diffusion coefficient at infinite dilution
$D(T,C)$	[cm^2/s]	Diffusion coefficient at non-infinite dilution
E_a	[J/mol]	Activation energy
F	[C/equiv]	Faraday, the value is 96,500
J_D	[mol/(cm^2·s)]	Flux of diffusion
J_R	[mol/(cm^2·s)]	Flux of reaction
$J_{R(n)}$	[mol/(cm^2·s)]	Reaction flux of species n
k	[cm/s]	Etching rate coefficient
k_1	[cm/s]	First order etching rate coefficient
k_2	[cm^4/(mol·s)]	Second order etching rate coefficient
M	[mol/kg]	Molality of solute
M_n	[g/mol]	Molecular weight of species n
n_+	(no unit)	Valence of cation
n_-	(no unit)	Valence of anion
R	[J/(mol·K)]	Gas constant, the value is 8.314
$R_{n(n=1\sim3)}$	[μm/min]	The etching rates to calculate A_1, A_2 and E_a
T	[K]	Temperature
$T_{n(n=1\sim3)}$	[K]	The temperatures to calculate A_1, A_2 and E_a
V_s	[cm^3/mol]	Partial molal volume of solvent
$y_\pm$	(no unit)	Molar activity coefficient of an electrolyte
ρ_n	[g/cm^3]	Density of species n
ρ_s	[mol/cm^3]	Molal density of solvent
ρ_0	[mol/cm^3]	Molal density of solution
δ	[cm]	Etching front distance
λ_+^0	[equiv/cm^3]	Limiting (zero-concentration) cation conductance
λ_-^0	[equiv/cm^3]	Limiting (zero-concentration) anion conductance
η	[cP]	Viscosity of solution
η_w	[cP]	Viscosity of water
η_s	[cP]	Viscosity of solvent
$\gamma_\pm$	(no unit)	Mean ionic activity coefficient of solute

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1. Introduction

Release etching of a sacrificial oxide layer is an important process in surface micro-electro-mechanical systems (surface MEMS) [1]. The etching rate of sacrificial layer depends on the concentration of etching solution, temperature, and structure being released [2,3]. Some models have been proposed to describe the etching process of silicon dioxide with hydrofluoric acid (HF) [4,5]. Up to now, the combined first-and-second order release-etching model presented by Monk [6] and Liu [7] seems the best to describe the etching process. For short time etching at room temperature, this model fits the etching process well. However, it is still not clear whether the model can fit the extended etching process at different temperatures.

In fabrication process of many important surface MEMS devices, the etching length of sacrificial layer can reach several hundred microns. Over etching is harmful to the polycrystalline silicon structure layer [6]. Therefore, precise prediction of the etching process will save the process time and protect the structure layer from over etching as well. In most of the existing release-etching models, the diffusion coefficient is considered as a constant even in the different bulk etchant concentrations and temperatures. Eaton [8] proposed that the value of diffusion coefficient varied with the bulk etchant concentration. However, the diffusion coefficient was still assumed as a constant during the whole etching process. It will be shown from both theory and experiments in this work that the assumption of diffusion coefficient as constant will cause large error during extended etching.

The existing first-and-second orders release-etching models are reviewed at the beginning of the paper. These models are referred as constant diffusion coefficient (CDC) models, since they consider the diffusion coefficient as a constant. The model is then modified by considering the diffusion coefficient as a function of temperature and HF concentration at the etching front. This model is referred as the modified model. The etching length and rate at different temperatures as functions of etching time are obtained by experiments. The results are compared with the models and some useful conclusions will be obtained.

2. Model of sacrificial layer etching

2.1. The CDC model

Modeling of release etching is based upon relationship among etchant diffusion flux, etchant concentration, and etching rate. Fig. 1 shows a channel structure being etched in HF solution, in which $\delta(t)$ is the etching front position as a function of etch time, C_b is the concentration of initial solution, and C is the concentration of HF at etching front, respectively.

The CDC model is proposed by Monk [6] and Liu [7]. They use simplified power law kinetics [9,10]. In the model, the following assumptions are used:

(1) All the liquid has a constant density,
(2) The effects of reaction products on the etching process are small enough,
(3) The diffusion is in steady state.

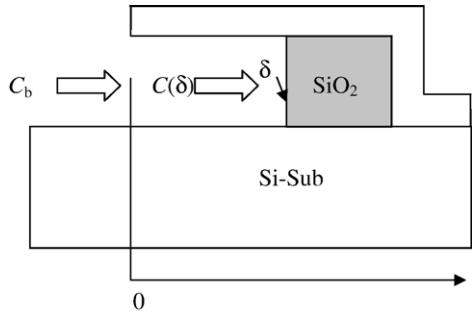

Fig. 1. Schematic of etching process in a channel structure. The initial HF concentration is C_b. The concentration outside the channel is assumed to be stable during the whole etching process. The concentration at the etching front, $C(\delta)$ changes during etching process.

By these assumptions, the concentration of etchant distributes linearly. The diffusion flux J_D, i.e., the flux of HF diffusing to the etching front, can be expressed as,

$$J_D = D\frac{C_b - C}{\delta(t)} \tag{1}$$

where D is the diffusion coefficient of HF solution. In power law model [9,10], the reactive flux is expressed as,

$$J_R = kC^n \tag{2}$$

where n is the reaction order between 1.0 to 2.0, k is the reaction coefficient representing relationship between the reactive flux and the etchant concentration. In the CDC model, J_R is simplified as,

$$J_R = k_1 C + k_2 C^2 \tag{3}$$

In which k_1 and k_2 are the reaction coefficients. k_1 represents the relationship between the reactive flux and the etching front concentration, k_2 represents the relationship between the reactive flux and the square of etching front concentration.

At steady state, the above two fluxes are equal to each other,

$$J_D = J_R \tag{4}$$

According to the reactive equation of sacrificial etching,

$$6HF + SiO_2 \Leftrightarrow H_2S_iF_6 + 2H_2O \tag{5}$$

The etching rate is proportional to J_R as follow [11],

$$\frac{d\delta}{dt} = (\alpha J_R)|_{x=\delta} \tag{6}$$

$$\alpha = \frac{1}{6}\frac{M_{SiO_2}}{\rho_{SiO_2}} \tag{7}$$