

MODELING CONVECTION DRIVEN WET CHEMICAL ETCHING USING A TOTAL CONCENTRATION METHOD

P Rath, J C Chai

Nanyang Technological University, Singapore

Abstract

A total concentration fixed-grid method is presented to model the convection driven wet chemical etching process. The proposed method is analogous to the enthalpy method used in the modeling of melting and solidification problems. A total concentration which is the sum of the unreacted etchant concentration and the reacted etchant concentration is defined. The governing equation based on the newly defined total concentration includes the interface condition. Hence the etchfront position can be found implicitly using the proposed method. The reacted concentration is used to predict the etchfront position while etching progresses. Since the grid size is fixed, there is no grid velocity unlike the case with existing moving grid approaches. Cartesian grids are used to capture the complicated etchfront evolved during etching. The etching process is assumed two-dimensional. The model assumes an infinitely fast reaction at the interface and the flow is assumed incompressible of Newtonian fluid. For demonstration purposes, a finite-volume method is used to solve the resulting set of governing momentum equations, the continuity equation and the convection driven mass diffusion equation with prescribed initial and boundary conditions. The effect of flow parameters- the Reynolds number and the Peclet number on the etch profile growth is studied.

Nomenclature

a	coefficient of the discretization equation	D	diffusion coefficient of etchant
c	unreacted etchant concentration	M_{Sub}	molar mass of substrate
c_R	reacted etchant concentration	m	stoichiometric reaction parameter
$c_{R,max}$	maximum reacted etchant concentration	Pe	Peclet number
c_T	total etchant concentration	Re	Reynold number
		β	dimensionless etching parameter

1. Introduction

Wet chemical etching (WCE) process is the selective removal of materials from the surface of a substrate by reaction with liquid chemicals to give a specific desired pattern on the substrate surface. The pattern structure is used for various purposes like the electronic circuitry in PCBs, the design of IC [1] and MEMS [2] devices, the design of shadow mask for color TV [3] etc. There are various existing approaches to model the WCE process under stationary and flowing etchant condition. The analytical approach is the asymptotic solution [4-6], which is applicable only for highly simplified cases. The numerical approaches includes the moving-grid (MG) approach [7-10], the variational inequality approach [7, 11], the level-set method [12, 13], and the recently introduced total concentration fixed-grid (FG) method [14, 15].

The moving grid (MG) method is the widely used numerical approach to model the WCE process. In the MG method, the computational domain generally changes with time due to the changing topology of the moving boundary. When the MG method applied to the WCE problem, the

computational domain is the etchant domain and it continuously expands with time because of the dissolution of substrate by the etchant. As the computational domain expands with time, the computational mesh has to be regenerated at every time step. Hence, an unstructured mesh system and body fitted grids are necessary to capture the etchfront accurately. This makes the method computationally very expensive and its implementation is not so straightforward.

The total concentration fixed-grid method proposed by Chai and his co-workers is extended in this article to model the WCE process when the etchant solution flows over the substrate surface. This method is analogous to the enthalpy method used to model melting/solidification problems [16, 17]. Convection plays an important role in etching deep cavities. The etch rate is much higher when the etchant flows over the substrate surface compared to etching by pure diffusion process. In convection driven etching, the continuity and momentum equations needs to be solved in addition to the mass diffusion equation. In the present method, total concentration is the sum of the unreacted and the reacted etchant concentration. The modified governing equation based on the total concentration includes the interface condition. The grid size is fixed, hence no grid velocity. Simple Cartesian grids are used to capture the complicated etchfront evolved by etching. The interface position can be found implicitly. The reacted concentration of etchant is a measure of the etchfront position. The effect of the flow parameters- the Reynold number and the Peclet number on the shape evolution of etch profiles is studied.

This article is divided into six sections. In the next section, a two-dimensional convection-diffusion WCE problem, the governing equations for flow and etchant concentration, the interface condition and the boundary conditions are described. Various ingredients of the method used in this article are briefly described. A brief description of the numerical method used in this article is given. The overall solution procedure is then summarized. Discussions of the results obtained using the proposed FG method are presented. Some concluding remarks are then given.

2. Problem Description and Governing Equations

The schematic and computational domain for the two-dimensional etching problem considered here is shown in Fig. 1. A cavity of width $2a$ is to be etched in a substrate (Fig. 1) partially protected by an inert mask. The solution containing the etchant molecules is flowing over the substrate to be etched. For demonstration purposes, the width of the mask on both sides of the cavity is assumed to be large enough so that the shear flow prevails far away from the cavity mouth to be etched. The flow is assumed incompressible of a Newtonian fluid with constant properties. Initially at $t = 0$, the concentration of the etchant in the flowing solution is zero. At $t > 0$, the etchant molecules with concentration c_o enters the cavity through left boundary Γ_1 as shown in Fig. 1. Reaction between the etchant and the substrate at the etchant-substrate interface results in the reduction of the concentration of etchant adjacent to the etchant-substrate interface and the depletion of the substrate. The reaction at the interface is assumed infinitely fast which makes the etchant concentration to zero at the interface. The governing equations for fluid flow and mass transfer, the interface condition and the boundary conditions are presented next.

Governing Equations

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0 \quad \text{in } \Omega(t) \quad (1)$$

$$\frac{\partial(\rho u)}{\partial t} + u \frac{\partial(\rho u)}{\partial x} + v \frac{\partial(\rho u)}{\partial y} = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad \text{in } \Omega(t) \quad (2)$$

$$\frac{\partial(\rho v)}{\partial t} + u \frac{\partial(\rho v)}{\partial x} + v \frac{\partial(\rho v)}{\partial y} = -\frac{\partial p}{\partial y} + \frac{\partial}{\partial x} \left(\mu \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial v}{\partial y} \right) \quad \text{in } \Omega(t) \quad (3)$$

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right) \quad \text{in } \Omega(t) \quad (4)$$

Initial and Boundary Conditions

$$\vec{U} = \vec{U}_0, c = 0 \quad \text{in } \Omega(0) \quad (5a)$$

$$u = ky, v = 0, c = c_0 \quad \text{at } \Gamma_1, t \geq 0 \quad (5b)$$

$$\frac{\partial u}{\partial x} = 0, v = 0, \frac{\partial c}{\partial x} = 0 \quad \text{at } \Gamma_3, t \geq 0 \quad (5c)$$

$$u = \text{Constant} = u_{\max}, v = 0, \frac{\partial c}{\partial y} = 0 \quad \text{at } \Gamma_2, t \geq 0 \quad (5d)$$

$$u = 0, v = 0, \frac{\partial c}{\partial \hat{n}} = 0 \quad \text{at } \Gamma_4(t) \text{ and } \Gamma_4(t), t \geq 0 \quad (5e)$$

$$u = 0, v = 0, c = 0 \quad \text{at } f(t), t \geq 0 \quad (5f)$$

where k in Eq. (5b) is the shear rate of the etching fluid.

Interface Condition on $f(t)$

$$\vec{v} = -\frac{DM_{Sub}}{m\rho_{Sub}} \nabla c \quad (6)$$

where \vec{v} is the velocity of the etchant-substrate interface, D is the diffusion coefficient of etchant, M_{Sub} is the molecular weight of the substrate, ρ_{Sub} is the density of the substrate and m is the stoichiometric reaction parameter of the etchant-substrate reaction.

3. The Total Concentration Method

The *total concentration* (c_T) of etchant is defined as

$$c_T \equiv c + c_R \quad (7)$$

where c is the unreacted etchant concentration and c_R is the reacted etchant concentration. Physically, c_R is the etchant concentration consumed in the reaction. As such it is constant except at the etchant-substrate interface. This is used to capture the etchfront implicitly. The value of c_R changes from 0 to its maximum possible value of $c_{R,\max}$ in a control volume where etching is taking place (known as the etching control volume – ECV). The $c_{R,\max}$ is given as

$$c_{R,\max} = \frac{m\rho_{Sub}}{M_{Sub}} \quad (8)$$

The modified governing equation using the total concentration is given as

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right) - \left(\frac{\partial c_R}{\partial t} + u \frac{\partial c_R}{\partial x} + v \frac{\partial c_R}{\partial y} \right) \quad (9)$$

Equation (9) is the modified mass diffusion equation valid in both the etchant and the substrate regions. The interface condition given by Eq. (6) is contained in Eq. (9). The derivation of the interface condition from the modified governing equation can be found in previous articles on this method [14, 15].

Procedure to Update c_R

An iterative procedure to calculate the reacted etchant concentration c_R is presented in this section. As the reacted concentration is constant away from the etchant-substrate interface, Eq. (9) reduces to the original governing equation (Eq. 4). In the proposed FG method, the control volumes where etching is taking place are identified and are called the etching-control-volumes (ECVs). The ECVs are the substrate control volumes adjacent to the etchant control volumes. The whole interface is captured in the ECVs. In an ECV, c_R changes from 0 to its maximum possible value of $c_{R,max}$. Since at the interface, the velocity of etchant is zero, hence inside the ECVs, the velocity components u and v will be zero. As a result, the iterative update equation of c_R remains the same as for stationary etchant solution. This is given as

$$c_{R,P}^{m+1} = c_{R,P}^m + \alpha a_P \frac{\Delta t}{\Delta V_P} c_P^m \quad (10)$$

where m is the m^{th} iteration of the current time step, P signifies the control volume, a is the coefficients of the discretization equation, α is the under-relaxation factor ($0 < \alpha \leq 1$), ΔV is the volume of a control volume and Δt is the time step size respectively. Within the ECVs where etching is taking place, the reacted concentration is updated using Eq. (10). A given ECV is said to be etched completely when $c_{R,P}^{m+1}$ reaches $c_{R,max}$.

4. Numerical Method

The finite volume method (FVM) of Patankar [18] is used to solve the governing equations for fluid flow and etchant concentration. A detailed discussion of the FVM can be found in Patankar [18]. The SIMPLE algorithm of Patankar [18] is used to solve the governing continuity and momentum equations. For convergence of the solution, a tolerance value is set for all the parameters computed iteratively. In the present study, the solution is deemed to be converged beyond a tolerance value which is set to 10^{-11} for mass conservation while solving the continuity and momentum equations, the maximum change in the unreacted and reacted etchant concentration over the whole computational domain while solving the mass diffusion equation.

5. The Overall Solution Procedure

The overall solution procedure for the proposed total concentration method can be summarized as follows:

1. Specify the etchant domain, the substrate domain and the mask region. Ensure that the etchant-substrate interface lies on the interface between two control volumes.
2. The etchant velocities are suppressed to zero in the substrate and the mask regions by using the “internal boundary condition” of Patankar [18].
3. Solve the steady state continuity and momentum equations (Eqs. 1-3) with prescribed boundary conditions (Eqs. 5b-5e) to get the initial velocity distribution (\vec{U}_o) in the whole etchant and substrate domain including the mask region.
4. Set the initial unreacted etchant concentration as zero in the etchant and the substrate domains including the mask region.
5. Initially set c_R to 0 in the substrate domain including the mask region and to $c_{R,max}$ in the etchant domain respectively.
6. Advance the time step to $t + \Delta t$.
7. Identify the etching control volumes (ECVs).
8. Use the “internal” boundary condition treatment of Patankar [18] to set the unreacted etchant concentration in the mask and substrate regions to zero.
9. Solve Eqs. (1-3) and Eq. (9) for the flowing solution and unreacted etchant concentration.

10. Update the reacted concentration in the ECVs using Eq. (10).
11. Check for the convergence.
 - a) If the solution has converged, then check if the required number of time steps has been reached. If yes, stop. If not, repeat (6) to (11).
 - b) If the solution has not converged, then check the calculated reacted concentration.
 - If $c_R < c_{R,max}$, repeat (9) to (11).
 - If, $c_R \geq c_{R,max}$ then set $c_R = c_{R,max}$ and repeat (7) to (11).

6. Results and Discussions

The schematic of a two-dimensional etching problem with flowing etchant solution is shown in Fig. 1. The non-dimensional width of the mask on both sides of the etching cavity is taken as $L_1 = l_1/a = 4.0$ and the dimensionless height of etchant is taken as $L_3 = l_3/a = 4.0$. The width and thickness of the substrate are taken as $L_{Sub} = 2(1 + L_1) = 10.0$ and $L_2 = l_2/a = 2.0$ respectively. Following dimensionless variables are used for presentation of results.

$$X = \frac{x}{a}, Y = \frac{y}{a}, t^* = \frac{tD}{a^2} \quad (11a)$$

$$u^* = \frac{u}{u_c}, v^* = \frac{v}{u_c}, C = \frac{c}{c_o}, C_R = \frac{c_R}{c_o}, P = \frac{p}{\rho u_c^2} \quad (11b)$$

$$Re = \frac{\rho u_c a}{\mu}, Pe = \frac{u_c a}{D}, \beta = \frac{m \rho_{Sub}}{c_o M_{Sub}} \quad (11c)$$

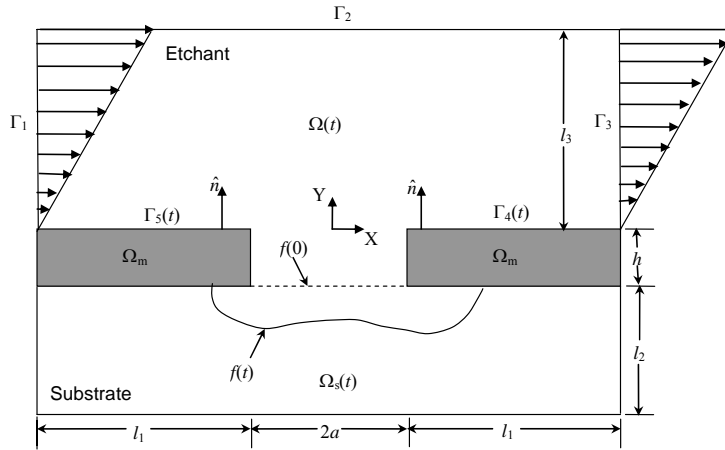


Figure 1. Schematic of the two-dimensional etching problem.

where Re is the Reynold number, Pe is the Peclet number, u_c is magnitude of the velocity at the center of the etch groove (at the origin as shown in Fig 1) and β is the dimensionless etching parameter.

A grid refinement study is performed to ensure the solutions to be grid independent. The Re and Pe values are taken as 0.1 and 100 respectively. The dimensionless shear rate ($k^* \equiv ka/u_c$) for these given set of flow parameters is 6.23. The dimensionless etching parameter is taken as $\beta = 100$ and thickness of the mask is $H = h/a = 0.5$. Figure 2 shows the evolution of etch profiles with three different grid sizes: 84×56 , 147×100 and 273×179 . From the time independent test, the time step size is found to be $\Delta t^* = 0.01$ for all the three grid sizes. It is seen that the grid sizes of 147×100 and 273×179 produced the same etchfronts at five different times as shown in Fig. 2. Therefore, 147×100 control volumes are used in this article for further presentation of results.

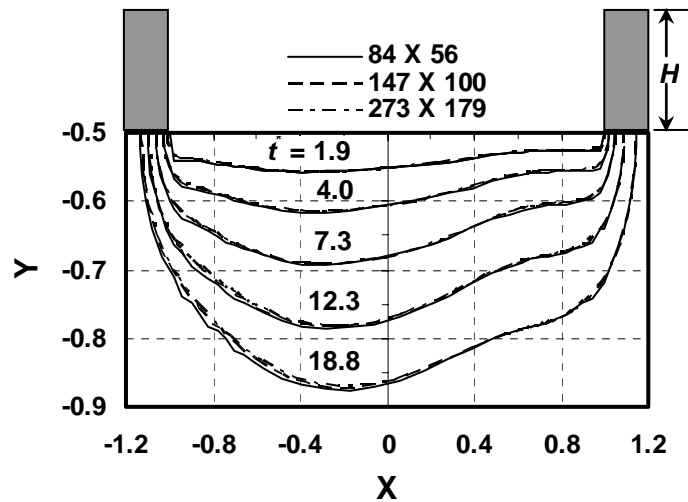


Figure 2. Grid independence study for $\beta = 100$ and mask thickness $H = 0.5$.

The etch profiles obtained from the present FG method are compared with the existing MG method as shown in Fig. 3. The flow and etching parameters are the same as stated above. It is seen that the etch profiles obtained using the FG method is in good agreement with the MG method. The etch profiles are very irregular in shape at the beginning. This is because of the highly non-uniform etchant concentration distribution due to the complicated flow pattern (shown in Fig. 4a) near the groove. At early etching time ($t^* < 18$), the underetching (etching below the mask) is more in the mask region towards the left of the centerline of the etching groove. The situation reverses at later times i.e. the etch rate and mask undercut are higher towards the right of the centerline.

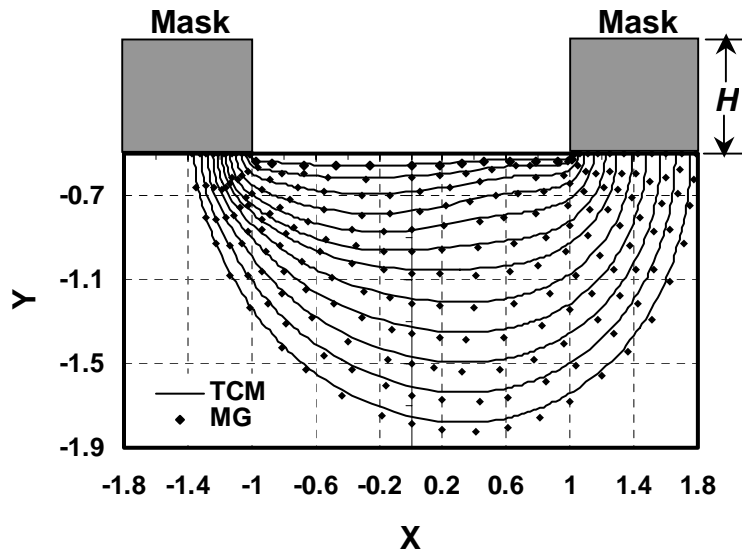


Figure 3. Comparison of etchfronts obtained from total concentration method (TCM) with the existing moving grid (MG) method for $\beta = 100$. The etchfronts are shown for dimensionless times $t^* = 1.9, 4.0, 7.3, 12.3, 18.8, 26.9, 34.7, 45.6, 56.7, 68.6, 81.5, \text{ and } 95.8$. The mask thickness is $1/4$ of the cavity mouth width ($H = 0.5$).

Figure 4 shows the flow pattern near the etching cavity region at early etching time and at later time for the above set of flow and etching parameters. Figure 4a shows the velocity distribution at an early etching time ($t^* = 4$) where weaker recirculating eddies are developed in the corner regions especially in the left corner. This is because of the low aspect ratio of the cavity where the etching fluid can easily penetrate through the cavity. However, at later times, due to the dissolution of the substrate by the etchant, the aspect ratio becomes larger and the external flow is incapable of penetrating the cavity. Hence, the recirculation eddies are more strong and clearly seen near the

center line of the cavity (as shown in Fig. 4b) and it gradually moves towards the right of the centerline. This explains why the etch rate is faster and the underetching is higher towards the right of the centerline of etching cavity at later times. Figure 5 shows the concentration distribution in the etching cavity region at $t^* = 95.8$. It is seen that the etchant concentration distribution is highly non-uniform near the center of the recirculation eddy. This is because of the complex flow pattern in the recirculation region.

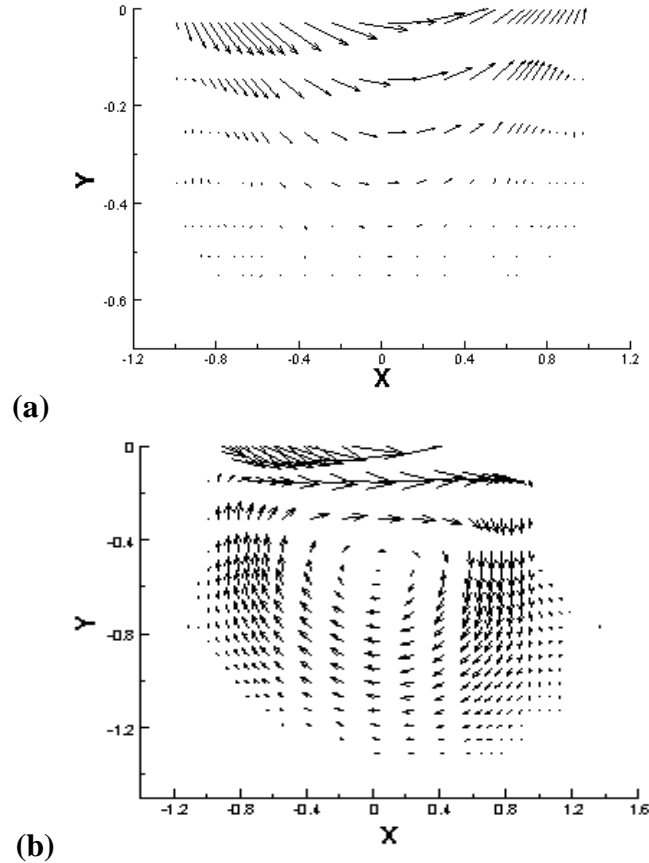


Figure 4. Velocity vector plot in the etched cavity region for $\beta = 100$ and the initial aspect ratio of $1/4$: (a) velocity vector plot at $t^* = 4.0$; (b) velocity vector plot at $t^* = 95.8$.

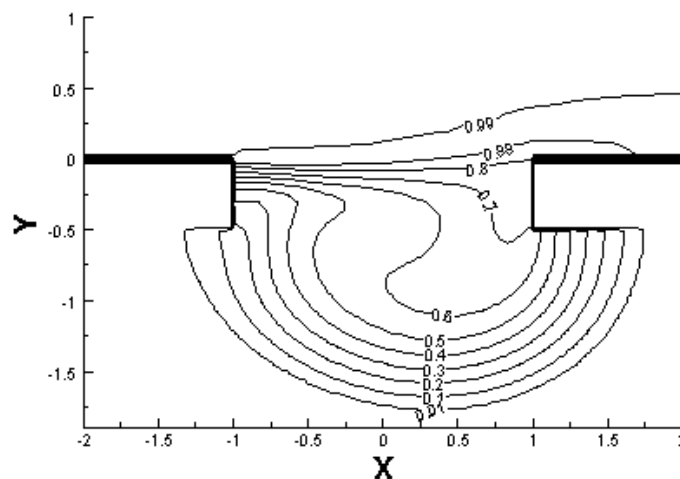


Figure 5. Concentration contours in the cavity region at $t^* = 95.8$ for $\beta = 100$ and initial aspect ratio of $1/4$.

Figure 6 shows the effect of flow parameters on the etch profile evolution while etching progresses. Three sets of flow parameters are taken to study this effect. For each value of Re a corresponding

value of Pe is chosen based on the properties of etching fluid. The properties of etching fluid are basically determined by the non-dimensional parameter called as Schmidt number (Sc), which is the ratio of Pe to Re . For a given etching fluid Sc is constant. For most of the etching fluids, the Sc is of the order of 10^3 [9]. The etching fluid enters the cavity through the left boundary Γ_1 with constant velocity u_{in} as shown in Fig. 6a. The velocity terms in the governing equations are non-dimensionalized using u_{in} . As a result, the flow parameters, Re and Pe are also based on u_{in} instead of u_c as defined earlier in Eq. (11c). As expected, with increase in the value of Re , the etch rate is faster and the profile goes deep as shown in Fig 6b. This is because the fresh etchant is more readily available at the interface with increased flow velocity of the etchant solution.

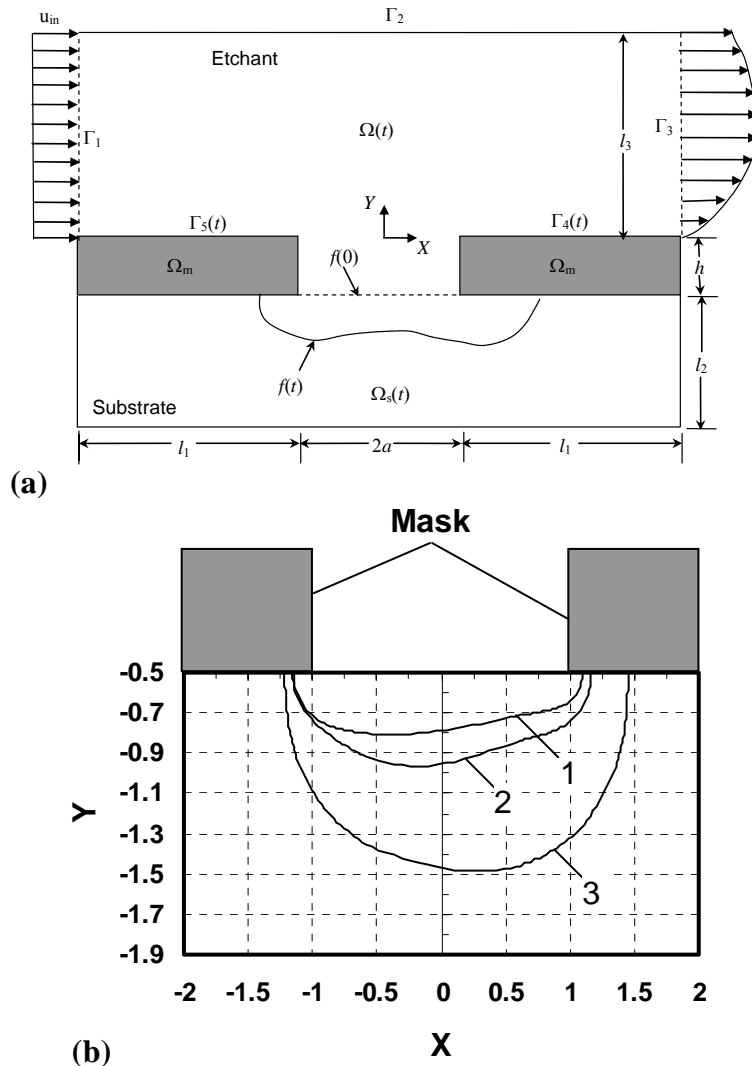


Figure 6. Effect of flow parameters on etch profile evolution: (a) modified schematic; (b) Etchfronts at $t^* = 20$ with $\beta = 100$ for three set of flow parameters: 1 - $Re = 0.1$, $Pe = 100$; 2 - $Re = 1$, $Pe = 1000$; 3 - $Re = 10$, $Pe = 10000$.

7. Conclusions

A fixed-grid method based on the total-concentration of etchant has been presented to simulate the convection driven WCE. The proposed method is analogous to the enthalpy method used to model melting/solidification processes. The modified governing equation based on the total concentration includes the interface condition. Simple Cartesian grids are used to predict the etchfront implicitly. The method has been applied to two-dimensional convection driven WCE with infinitely fast reaction at the interface. For demonstration purposes, the finite-volume method is used to discretize the governing equation. The effect of Re on the etch profile evolution is studied. As the Re value

increases, the flow velocity of etchant fluid increases, which leads to high etch rate and deep etched cavity can be formed.

References

1. Madou, M. J., 2002, Fundamentals of Microfabrication, 2nd Edition, CRC Press, New York.
2. Mastrangelo, C. H. *et al.*, 1995, Surface Micromachined Capacitive Differential Pressure Sensor with Lithographically-Defined Silicon Diaphragm, The 8th International Conference on Solid-State Sensors and Actuators, Eurosens IX (Stockholm June 25-29), 612-615.
3. Hoffman, K. H. and Sprekels, J., 1990, Free Boundary Problems: Theory and Applications, Longman Scientific and Technical, 1, 89.
4. Kuiken, H. K., 1984, Etching: A Two-Dimensional Mathematical Approach, Proceedings of the Royal Society of London A, 392, 199-225.
5. Kuiken, H. K., 1984, Etching Through A Slit, Proceedings of the Royal Society of London A, 396, 95-117.
6. Kuiken, H. K. *et al.*, 1986, Etching Profiles At Resist Edges - I. Mathematical Models For Diffusion-Controlled Cases, Journal of the Electrochemical Society, 133, 1217-1226.
7. Vuik, C. and Cuvelier, C., 1985, Numerical solution of an etching problem, Journal of Computational Physics, 59, 247-263.
8. Shin, C. B. and Economou, D. J., 1989, Effect of Transport and Reaction on the Shape Evolution of Cavities During Wet Chemical Etching, Journal of the Electrochemical Society, 136, 1997-2004.
9. Shin, C. B. and Economou, D. J., 1991, Forced and Natural Convection Effects on the Shape Evolution of Cavities During Wet Chemical Etching, Journal of the Electrochemical Society, 138, 527-538.
10. Driesen, C. H., 1999, Simulation of Convection-Driven Wet-Chemical Etching, PhD. Thesis, University of Twente, The Netherlands.
11. Bruch Jr., J. C. *et al.*, 1993, Parallel Computing Used in Solving Wet Chemical Etching Semiconductor Fabrication Problems, GAKUTO International Series, Mathematical Sciences and Applications, 1, 281-292.
12. Adalsteinsson, D. and Sethian, J. A., 1995, A Level Set Approach to a Unified Model for Etching, Deposition and Lithography I: Algorithms and Two-Dimensional Simulations, Journal of Computational Physics, 120, 128-144.
13. La Magna, A. *et al.*, 2003, Computational Analysis of Etched Profile Evolution for the Derivation of 2D Dopant Density Maps in Silicon, Materials Science and Engineering B, 102 (1-3), 43-48.
14. Rath, P. *et al.*, 2005, A Fixed-Grid Approach for Diffusion- and Reaction-Controlled Wet Chemical Etching, International Journal of Heat and Mass Transfer, 48, 2140-2149.
15. Rath, P. *et al.*, 2005, Modeling Two-Dimensional Diffusion-Controlled Wet Chemical Etching Using A Total Concentration Approach, International Journal of Heat and Mass Transfer, in press.
16. Shamsundar, N. and Sparrow, E. M., 1975, Analysis of Multidimensional Conduction Phase Change via the Enthalpy Method, Journal of Heat Transfer, 97, 333-340.
17. Voller, V. and Cross, M., 1981, Accurate Solutions of Moving Boundary Problems Using the Enthalpy Method, International Journal of Heat and Mass Transfer, 24, 545-556.
18. Patankar, S. V., 1980, Numerical Heat Transfer and Fluid Flow, 1st edition, Hemisphere, New York.