HOMOGENIZATION OF DROP STAIN BY RADIAL ELECTROOSMOTIC FLOW IN AN EVAPORATING DROP

Sung Jae Kim*, Kwan Hyoung Kang**, In Seok Kang*, and Byung Jun Yoon*
*Department of Chemical Engineering, Division of Mechanical and Industrial Engineering, Pohang University of Science and Technology, Pohang 790-784, Kyungbuk, Korea
**Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's college road, Toronto, M5S 3G8, Canada

1. Introduction

Dynamics of evaporating droplet on a solid substrate have been emphasized in the scientific field such as heat transfer applications and commonly observed in everyday life such as ring-like stain after evaporating coffee droplet. Recently, the simple phenomena came out to be essential mechanism in the field of bio and analytical chemistry applications during past few decades especially in the case of open environment. However, unexpected ring pattern stain formation after complete evaporation of droplet has become a key obstacle for a distinct analysis. Such localization of solute may hinder accurate analysis of drop sample, and it is desirable to devise a scheme for homogenizing the solute distribution inside a drop after complete evaporation. Physicochemical mechanism of drop stain phenomenon has yet to be developed, but the contact line pinning due to hydrophilic surface and the non-uniform evaporation from the edge of the droplet might contribute to the outward migration of solute [1]. As the droplet remains pinned on the substrate and the liquid is removed from the edge of droplet, the outward flow from the interior must replenish the mass loss. The spotlighted explanation for the evaporation from the edge is the probability of escaping an evaporating molecule at the edge is higher than at the center due to the geometrical curvature of droplet [2].

In this work we study the utility of radial electroosmotic flow as an effective mean for controlling outward flow inside the droplet. We devise the circular electrode system which also has point electrode in the center of circle. The electric field developed between the center electrode and the circular electrode placed along the drop rim causes a radial electroosmotic flow in the vicinity of the bottom of droplet. By changing the polarity and the applied voltage, we can control the strength and direction of the radial electroosmotic flow, and thus we can modify the solute distribution inside the droplet. With this device, the homogeneous deposition on a substrate is possible and the solutes are, even, collected into the center of droplet according to the applying voltage. We also derive the analytical solution for the flow inside the droplet where there is the radial electroosmotic flow so that verify the experimental condition for the best stain homogeneity.

2. Theory

To obtain the flow field inside the droplet caused by the non-uniform evaporation

and electroosmotic velocity, body forces should include the two factors. Non-uniform evaporation effect can be fairly inserted in the pressure gradient term. However, the consideration of the electroosmotic body force term to the governing equations is difficult due to the electrical double layer. Actually, the electroosmotic flow of electrolytes is caused by electrostatic body force exerted on electrical charge in the electrical double layer formed near the surface. In many cases, the electrical double layer thickness is much smaller than the system dimensions, and most of previous studies dealt the electroosmotic flow with specifying slip velocity condition determined by the Helmholtz-Smoulochowski equation, $\mathbf{u}|_s = -\varepsilon \zeta \mathbf{E}/\mu$, at the surface. Here, ε, ζ, and $\mathbf{E}$ are the liquid permittivity, the zeta potential of the contact surface and the applying electric field, respectively. The slip velocity on the surface is applied to solve the Stokes equation instead of typical no-slip velocity boundary conditions. To obtain the slip condition, we need to know the non-uniform electrical field distribution. Usually, include our system, the electrical field is negative gradient of electric potential due to external electrode, $\mathbf{E} = -\nabla \phi$, and the electrical potential is governed by the Laplace equation, $\nabla^2 \phi = 0$ in given coordinate system.

3. Mathematical model

A small droplet of water, whose shape is spherical cap, on a substrate is presented in Figure 1. Due to the axial symmetry, the droplet system can be described with a cylindrical coordinate system with radial coordinate r and axial coordinate z.
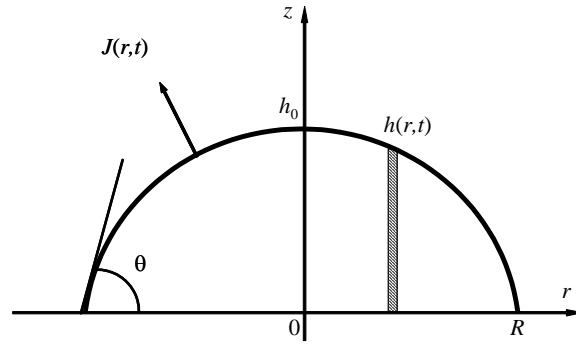

Figure 1. A schematics of spherical droplet on a substrate.

The local height $h(r,t)$ of spherical droplet is determined from the contact angle θ and the contact radius R. In previous studies, various non-uniform flux forms due to the evaporation are presented. In this work, we use the simple flux form which is given by Deegan et al. [1] and is verified by Larson et al. [3]. Under these conditions, Deegan et al. obtained a height-average radial velocity field in an evaporating droplet which is

$$\overline{u}_r(r,t) = \frac{1}{4}\frac{1}{1-t_f}\frac{1}{\tilde{r}}\left[\left(1-\tilde{r}^2\right)^{-\lambda(\theta)} - \left(1-\tilde{r}^2\right)\right] \tag{1}$$

where t_f is the total drying time [2]. Using this 1-dimensional equation, Larson et al. derived the radial and axial velocity components under assumption that lubrication approximation,

the zero-shear stress boundary condition on the free air-liquid interface and the no-slip boundary condition on the substrate [4]. First, they assumed that the radial velocity u_r has parabolic in z-direction at each value of r and substituted u_r to the continuity equation for obtaining the axial velocity field u_z.

As the evaporation proceeds, the electrolyte concentration inside the droplet is increased and it makes the electrical double layer thinner. Since the DC electric field is applied and typical slip velocity condition is applicable when the electrical double layer is very thin, we can use the time-independent slip velocity condition if initial electrolyte concentration is reasonably high. We will treat the evaporating droplet system under a thin double layer condition in both theoretical and experimental study. To apply the slip-velocity boundary condition due to the electroosmosis, we should determine the electrical field distribution in the vicinity of the substrate surface. Figure 2 shows the schematic configuration of the center and rim electrode near the evaporating droplet bottom.
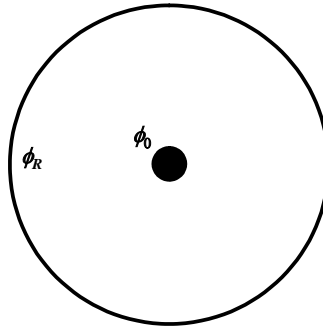

Figure 2. A schematics of center and circular electrode system.

ϕ_0 and ϕ_R are the electrical potential at the center and the rim electrode. The electrical potential distribution follows the Laplace equation in the polar coordinate and is logarithmic function. Because the electric field is fairly equal to the negative gradient of electrical field, the non-uniform electrical distribution is proportion to $1/r$. Consequently, the strength of electric field at the center is stronger than at the rim of droplet. When the slip-velocity condition is applied, u_r and u_z is given by

$$\tilde{u}_r = \frac{3}{8}\frac{1}{1-\tilde{t}}\frac{1}{\tilde{r}}\left[\left(1-\tilde{r}^2\right)-\left(1-\tilde{r}^2\right)^{-\lambda(\theta)}\right]\left(\frac{\tilde{z}^2}{\tilde{h}^2}-2\frac{\tilde{z}}{\tilde{h}}\right)+\frac{\alpha}{\tilde{r}}, \tag{2}$$

$$\tilde{u}_z = \frac{1}{4}\frac{1}{1-\tilde{t}}\left[1+\lambda(\theta)\left(1-\tilde{r}^2\right)^{-\lambda(\theta)-1}\right]\left(\frac{\tilde{z}^3}{3\tilde{h}^2}-\frac{\tilde{z}^2}{\tilde{h}}\right)$$
$$+\frac{3}{2}\frac{1}{1-\tilde{t}}\left[\left(1-\tilde{r}^2\right)-\left(1-\tilde{r}^2\right)^{-\lambda(\theta)}\right]\left(\frac{\tilde{z}^2}{2\tilde{h}^2}-\frac{\tilde{z}^3}{\tilde{h}^3}\right)\tilde{h}(0,t). \tag{3}$$

where α is the average strength parameter of the electroosmotic velocity determined from the following:

$$\alpha = \frac{\varepsilon\zeta|\mathbf{E}|}{\mu}\frac{t_f}{R}\left(\frac{1}{R}\int_0^R \frac{1}{r}dr\right)^{-1}. \tag{4}$$

And here the dimensionless variables are defined as follows:

$$\tilde{r}=\frac{r}{R},\ \tilde{z}=\frac{z}{h_0},\ \tilde{h}=\frac{h}{h_0},\ \tilde{t}=\frac{t}{t_f},\ \tilde{u}_r=\frac{u_r t_f}{R},\ \tilde{u}_z=\frac{u_z t_f}{h_0}.$$

On the substrate, the radial velocity exactly is exactly proportionate to the electrical field and the strength is controlled by the surface zeta potential and the external electric field strength. And also $1/r$ term satisfy both the continuity and Stokes equation because the differentiation of $r \times \alpha/r$ with respect to r vanishes to zero. Finally, we can use the full 2-dimensional velocity field given in equation (2) and (3) when the radial electroosmotic flow is applied.

Lastly, we should compute mass transfer problem for monitoring the solute deposition inside the droplet. Although we obtain analytical solution of the flow field inside the droplet as equation (2) and (3), we carry numerical analysis for the solute concentration, $c(r,z,t)$. We employ 2-dimensional model for solute distribution in this works due to the discrepancy between one dimensional model and our experimental results. The equation of solute conservation without diffusion is

$$\frac{\partial}{\partial\tilde{t}}\left(c\tilde{h}\right)+\frac{1}{\tilde{r}}\frac{\partial}{\partial\tilde{r}}\left(\tilde{r}c\tilde{h}\tilde{u}_r\right)+\frac{\partial}{\partial\tilde{z}}\left(c\tilde{h}\tilde{u}_z\right)=0. \tag{5}$$

This equation is solved using the symmetry condition at the origin and no net flux across into the substrate.

4. Experimental method

The present research used a silicon wafer to fabricate the circular electrode system. Prior to micro-fabrication of the silicon wafer, the wafer was cleaned to remove contaminations. Figure 3 provides a schematic illustration of the simplified fabrication process and used masks. Initially, the surface of wafer was oxidized to prevent a short circuit. A thin layer of positive film was then used as a mask shown as Figure 3(b) in the sputtering of center aluminum electrodes. The patterned aluminum was sputtered to form $1\mu m$ height electrode. We designed the center electrode such that it could be buried beneath the circular electrode. Thus the silicon insulation layer was deposited to prevent the short circuit using negative film mask shown in Figure 3(c) and exposed both point center electrode and rectangular connection pod for the purpose of supplying power source. Finally, the circular patterned aluminum electrode and its pod were deposited to $1\mu m$ height using positive mask shown in Figure 3(d).

We employed a particle tracer method to measure the deposition pattern of drop stain. Colloidal suspension of surfactant free, charge-stabilized, 50nm polystyrene micro-

spheres in NaCl 0.01M solution was used as the tracer. NaCl solution as an electrolyte formed a droplet to induce electroosmotic flow and the electrical double layer thickness is less than 10nm at the concentration. We can consider the thickness as thin double layer to applying the slip-velocity flow boundary condition. The electrophoretic motion of the tracers was negligible because the suspension is charge-stabilized. Although gravitational force and temperature gradient did not play important role in formation of ring stain [2], we kept horizontality of substrate and room temperature conditions during the experiments. The performance of the circular electrode was explored using a digital camera (PENTAX Optio4) in every 30 seconds. Micro-pipette was used to accurate drip a droplet of volume 1μL at the 1mm radius circular electrodes which mean a contact angle of π/3 under assumption that shape of droplet is spherical cap. Under those conditions, the dripped droplet completely evaporated within 20 minutes. The experiments carried at various applying voltages to investigate the effect of radial electroosmotic flow field.
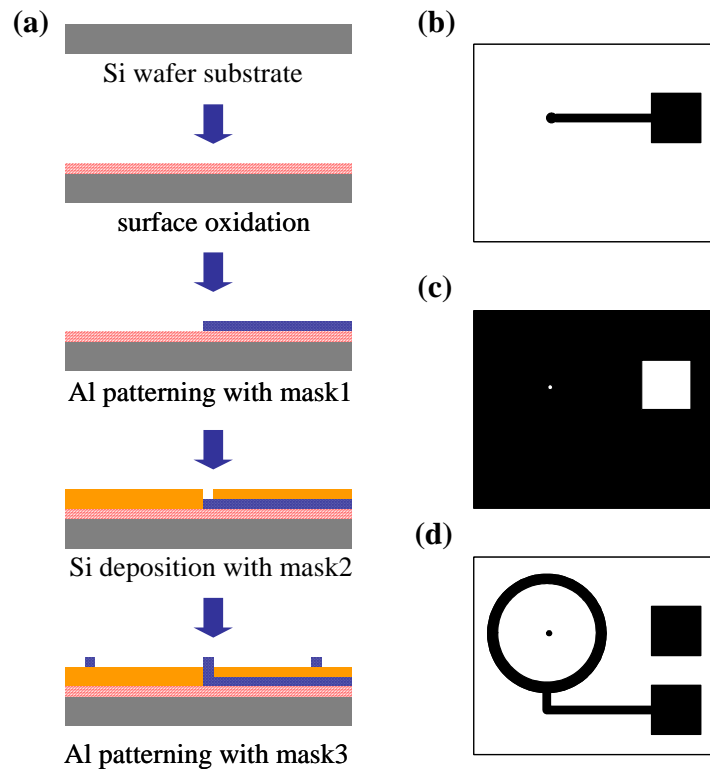

Figure 3. Process flow of electrode system and 3 used masks.

5. Results and discussions

The stream line inside the droplet and experimental results are shown in Figure 4 at the voltage of inducing a stronger outward radial electroosmotic flow. The strength parameter of electroosmotic flow, α is 0.025 (E=600V/m). And the flow may help a transport the solute to the edge. Consequently, thicker deposition in case of various outward electroosmotic flows is shown in Figure 4 (b) and (c).

In contrast to outward flow, Figure 5 shows the stream line when there is an inward

radial electroosmotic flow with α=-0.025. The stream lines separate around r=0.4 also due to the stronger inward electroosmotic flow near the center. In this inward case, important features are observed according to the strength of electroosmotic flow. At the weak electric field, the ring shaped solute deposition around the edge is fairly similar to the case of natural drying. As the strength of electric field is increase, the particles form uniform deposition at one moment and gradually get together into the center of droplet. When α is -0.025, we obtain homogeneous deposition pattern shown in Figure 5(b) and the solute would rather concentrate in the center than along the edge over the strength.
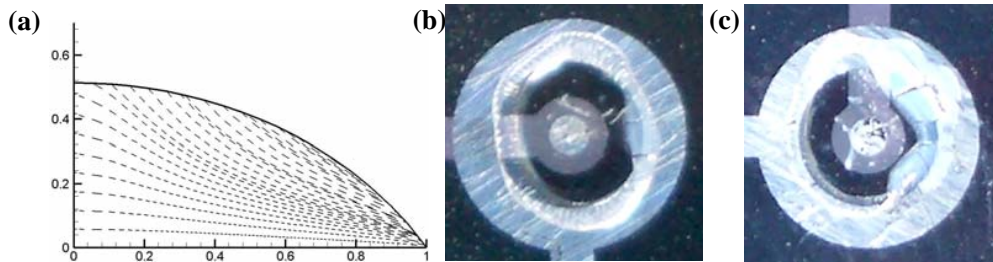

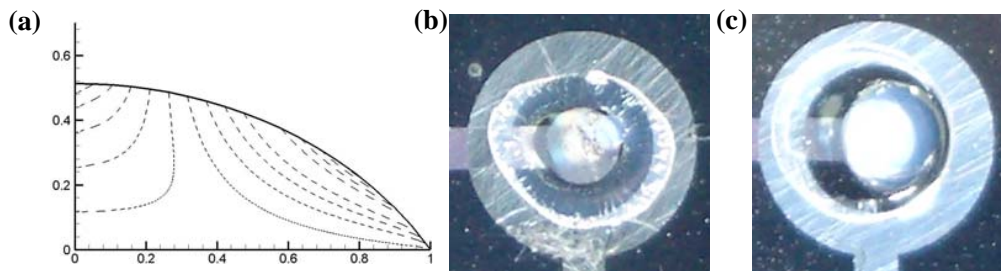Figure 4. Streamlines and stain after complete drying at outward electroosmotic flow condition.

Figure 5. Streamlines and stain after complete drying at inward electroosmotic flow condition.

For the detailed investigation for the uniform deposition, we compute the solute distribution at various values of α. The result is plotted in Figure 6 as a function of α at t=0.7 since the calculation diverges over t=0.7 for relatively large values of α. The deposition at the edge diminishes as the strength of electroosmotic flow turn to negative values. Actually, we can not numerically realize the phenomena shown in Figure 5(c) for large negative α value because the mass transfer equation (5) easily diverged. However, we can obtain relatively homogeneous deposition profile around the α=-0.025. The experimental slip velocity value using the Smoluchowski equation is about 43μm/sec (using E=-600V/m and water quantity at room temperature) under assumption ζ potential is -100mV. Although the ζ potential varies large caused from lots of fact such as kind of substrate and pH of electrolyte, etc, the value of -100mV is fairly reasonable within the error bound. When we test the theoretical interpretation of α, we use radial average of electroosmotic velocity due to the velocity is a function of radial position.
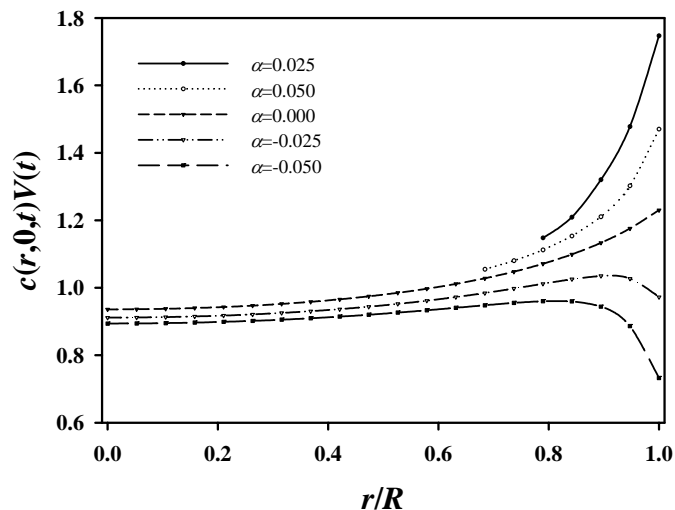
Figure 6. Concentration distribution profiles at various values of α.

Although the integration of $1/r$ from origin to edge used for calculating the average velocity diverges at r=0.0, we do not integrate from the origin. Fortunately, the real center electrode occupies certain area in the contrary to point electrode in theory. At α=-0.025, the theoretical average velocity is about 42μm/sec (t_f=20min, R=1mm, integration of $1/r$ from 0.2 to 1). This value is well agreed with the relevancy of the theoretical and experimental results.

6. References

[1] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, *Science*, 1997, **389**, 827-829.

[2] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, *Phys. Rev. E*, 2000, **62**, 756-765.

[3] H. Hu and R. G. Larson, *J. Phys. Chem. B*, 2002, **106**, 1334-1344.

[4] M. Chopra, L. Li, H. Hu, M. A. Burns, and R. G. Larson, *J. Rheol.*, 2003, **47**(5), 1111-1132.