

Effects of Solvents on Dissolution of Photoresist in Parylene Microchannels

Hatice Ceylan Koydemir^{*,**}, Haluk Kùlah^{*,***}, Canan Özgen^{**}, İsmail Tosun^{**}

^{*} MEMS Center, Middle East Technical University (METU), 06800, Ankara, Turkey,

^{**} Department of Chemical Engineering, METU, 06800, Ankara, Turkey,

^{***} Department of Electrical and Electronics Engineering, METU, 06800, Ankara, Turkey,

hceylan@metu.edu.tr, kulah@metu.edu.tr, cozgen@metu.edu.tr, itosun@metu.edu.tr

ABSTRACT

This paper presents a study for the effects of different types of solvents on dissolution of photo resist inside the parylene micro channels. Theoretical and experimental studies were carried out to model the dynamic behavior of the dissolution. In this account, dissolution rate expressions were derived by taking into account the reaction of resist with the solvent. Micro channels with a cross section of 15 μm x 50 μm were fabricated by encapsulating photo resist inside the parylene layers and using glass wafer as substrate. Experimental results indicated that photo resist dissolution in dipolar aprotic solvents was much faster than the other types of solvents. This finding can be used to select alternative chemicals for stripping encapsulated photo resist.

Keywords: Dissolution of photo resist, Parylene C, micro channel, microfluidics.

1 INTRODUCTION

Micro channels are the essential parts of lab-on-a-chip systems due to their capabilities in fluid directing and controlling at various fields, such as heat exchangers [1-2] and diagnosis assays [3-5].

The micro fabrication of channels with desired length and dimension is a critical issue and it necessitates good knowledge about the materials and the fabrication processes. In the prototyping of lab-on-a-chip systems, polydimethylsiloxane (PDMS) is preferred due to its simplicity and rapid prototyping fabrication process [6]. However, it is not compatible with batch fabrication processes, such as micro-electro-mechanical systems (MEMS) and integrated circuit (IC) technology. Parylene C is a good alternative as a polymer in forming channels due to its several properties, such as biocompatibility, compatibility with mass production processes and conformal coating [7-9]. There are many different techniques for fabricating parylene microfluidic channels utilizing different materials. One of the most common techniques is based on the encapsulation of photo resist between a substrate (glass, silicon, etc.) and the parylene. Photo resist is used as a sacrificial layer to form patterns, such as reservoirs, channels, and junction points. After deposition of Parylene C on top of photo resist, the inlet

and outlet reservoirs of the channels are opened by using plasma-etching processes and the dies are immersed into a solvent to allow flow in micro channels. However, the removal of photo resist from micro channels is a time consuming process and the complete removal of the photo resist may take days, depending on the length and dimensions of the channel. There are several commercial products as photo resist strippers. However, their usage in the removal of encapsulated photo resist is limited because of low dissolution rates and possibility to attack metals in long time. As an alternative, acetone which is commonly found in each clean room and/or laboratory was studied by Tai's group due to its selectivity [10].

In this study, the aim is to suggest a selection of alternative solvents for the dissolution of resist inside the micro channels. For this purpose, the dissolution of photo resist inside the micro channels was modeled as a quasi-steady-state process. Then, experimental studies were conducted with nine different solvents by taking into consideration the changes in the physical properties of the solvents.

2 THEORETICAL STUDIES

When the photo resist (A) encounters with the liquid (B), the molecules of A penetrate into the solution and undergo an irreversible first-order chemical reaction with a rate constant, k (Figure 1). The concentrations of reaction products do not interfere with the diffusion A through B, i.e., pseudo-binary behavior. When $\frac{Dt}{L}$ becomes much higher than one, the system can be treated as at pseudo-steady state.

The governing equation describing the dissolution process is as follows,

$$\frac{d}{dx} \left(D_{AB} \frac{dC_A}{dx} \right) - kC_A = 0 \quad (1)$$

Equation (1) was to be solved with boundary conditions:

(1) The concentration of the photo resist at the photo resist surface where it encounters with solvent was equal to the saturation concentration of photo resist in the solvent (C_{Ao}),

(2) The concentration of photo resist in the bulk solvent was equal to zero.

Finally, following equation has been obtained,

$$\cosh(L\sqrt{k/D_{AB}}) = \exp\left(\frac{C_{A0}M_A}{\rho_A}kt\right) \quad (2)$$

Then, a quasi-steady state model for the diffusion and chemical reaction of photo resist in solvent was developed to derive an expression for the length of cleared region inside the channel with time, for small and large values of $L\sqrt{k/D_{AB}}$ (Equations 3 and 4, respectively) and to figure out the parameters that influence the dissolution rate.

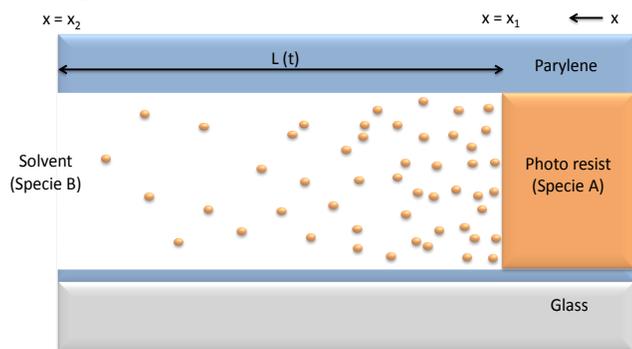


Figure 1: Schematic view of dissolution of photo resist in Parylene C microchannel.

$$L^2 = \frac{2}{k/D_{AB}} \exp\left(\frac{C_{A0}M_A}{\rho_A}kt\right) - 1 \quad (3)$$

$$L = \frac{1}{\sqrt{k/D_{AB}}} \left(\ln 2 + \ln \frac{C_{A0}M_A}{\rho_A} k \right) + \frac{1}{\sqrt{k/D_{AB}}} \ln t \quad (4)$$

where, L is the length of cleared region [m], k is the reaction rate constant [s^{-1}], D_{AB} is the diffusion coefficient [m^2s^{-1}], M_A is molecular weight [$kgmol^{-1}$], ρ_A is the density of photo resist [kgm^{-3}], and t is the time [s]. The parameters affecting the dissolution rate of photo resist are obtained as k , D_{AB} , and C_{A0} from the Equations (1) and (2). In the following section, the effects of these parameters on the dissolution rate will be analyzed.

3 EXPERIMENTAL STUDIES

The test structures with Parylene C micro-channels, which have a channel cross-section of $15 \mu m \times 50 \mu m$ and length of one centimeter, were fabricated by using surface micromachining processes.

Figure 2 shows the process flow for the fabrication of micro-channels. The process requires only one mask for lithography process. Glass wafer was used as substrate to enable the visualization of photo resist inside the micro channels. The glass wafer was cleaned with piranha solution and buffered hydrofluoric acid to remove organic residues and to increase the surface roughness for better adhesion of Parylene C (Figure 2a). Then, Parylene C was

coated to have two-micrometer thickness using PDS-2010 (Specialty Coating Systems, US). The adhesion promoter, A-174 silane was used to have better adhesion between glass wafer and Parylene C (Figure 2b). Then, AZ@9260 (520 cp) with $15 \mu m$ thickness was patterned according to the instructions of the manufacturer (Figure 2c). Next, five-micrometer thickness of Parylene C was coated to form channels (Figure 2d). Lastly, wafer was diced to have individual dies.

The solvents used in the experiments are given in Table 1. The solvents were selected such that, their physical properties (i.e., density, boiling temperature and melting temperature), which are directly related with the magnitude of diffusion coefficient, should make a comparison between the values.

Other than the solvent types, the parameters that affect the photo resist characteristics, such as UV exposure and temperature that change the physical properties of chemicals were also considered in the experiments.

The experiments were performed at room temperature, of 293 K. A die was placed in a glass dish with a cover to decrease evaporation of solvent. The change in the length of the cleared region of microchannel was recorded by taking colored photos with the digital camera of the microscope for 100 minutes with one-minute time interval. Then, the data analysis was performed.

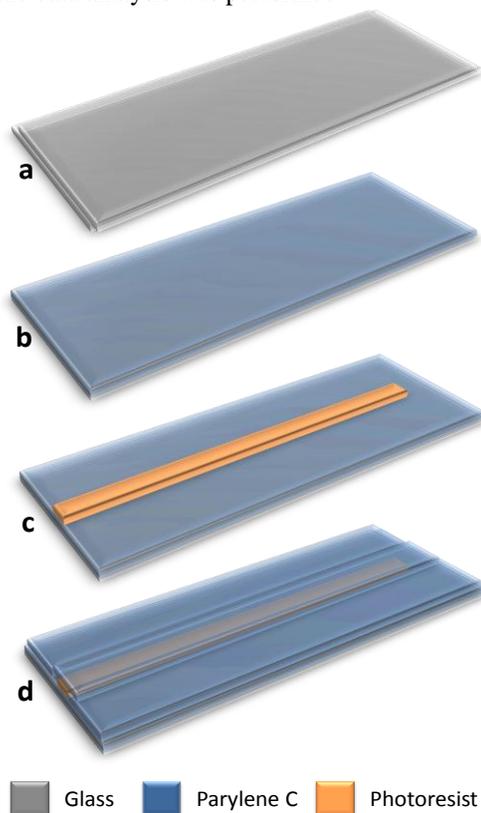


Figure 2: Fabrication flow: (a) Wafer cleaning, (b) Parylene C deposition, (c) Patterning with photo resist, (d) Parylene C deposition and dicing.

	Solvent	ρ (kg/m^3)	BP (K)	MP (K)
Organic solvents	N-heptane	679	371	182
	Cyclohexane	774	354	280
Dipolar aprotic solvents	Acetonitrile	776	355	227
	Acetone	784	329	178
	Ethyl acetate	895	350	189
	N-butyl acetate	876	399	195
	Dimethylsulfoxide (DMSO)	1095	462	291.5
	Dimethylformamide (DMF)	944	426	212
	N-methyl-2-pyrrolidone (NMP)	1026	475	249

Table 1: Types and some physical properties of the solvents.

4 RESULTS AND DISCUSSION

Firstly, experiments were carried out by using organic solvents (i.e., n-heptane and cyclohexane). However, the results indicated that, the dissolution rates of n-heptane and cyclohexane were too low thus; there was no change inside the channels after one hour (data not shown). Then, the dissolution rates with the immersion of individual dies into other solvents were examined and it was observed that dipolar aprotic solvents demonstrated an increase in the length of cleared region with time (Figure 3).

The rate of photo resist dissolution for the first 10 minutes was higher than the one for the last 10 minutes. Among the polar aprotic solvents studied, acetone had the highest dissolution rate while, DMSO was the solvent with the lowest dissolution rate at room temperature. This can be due to the low boiling temperature and low viscosity of the acetone compared to DMSO. The dissolution rate in increasing order was as follows: DMSO < NMP < n-butyl acetate < acetonitrile < ethyl acetate < DMF < acetone. There was no boundary region, which separates the photo resist from the cleared region after about 25 and 55 minutes for n-methyl-2-pyrrolidone and ethyl acetate, respectively. Therefore, further data could not be taken.

Then, the effect of UV exposure was analyzed by exposing the dies to 100, 300, and 999.9 mJ/cm^2 via using CL – 1000 UV Crosslinker (UVP LLC, US) before immersing the die into solvent. Figure 4 demonstrates that there is a slight effect of UV exposure (i.e., 3% difference between the final lengths of cleared regions) in release rate as it is expected.

The three different mixtures of acetone and DMSO (20% acetone, 40% acetone, and 60% acetone [v/v]) were prepared to see the effect of mixing on dissolution rate at room temperature. As shown in Figure 5, dissolution rate of acetone alone was higher than the others although the mixing percentage with acetone increases the dissolution

rate. The increase in dissolution rate in mixtures is due to the decrease in boiling point temperature and density.

Moreover, the dissolution rate can be increased by increasing temperature of the solvent, which decreases viscosity and density of the solvent. Thus, DMSO with high boiling temperature (462K) was heated up to 353K. 353K was selected so that the Parylene C layer will not be damaged with temperature, since the glass transition temperature of Parylene C is between 353K and 373K [11]. It was found that, the dissolution rate at 353K with DMSO was 2.4 fold greater than the one at 293K (Figure 5). The use of DMSO as an alternative to acetone can be preferred since the evaporation rate of DMSO even at 353K is too low and that renewal of the solvent is not necessary. The increase of temperature further will also increase the dissolution rate since the boiling point temperature of photo resist is around 413K.

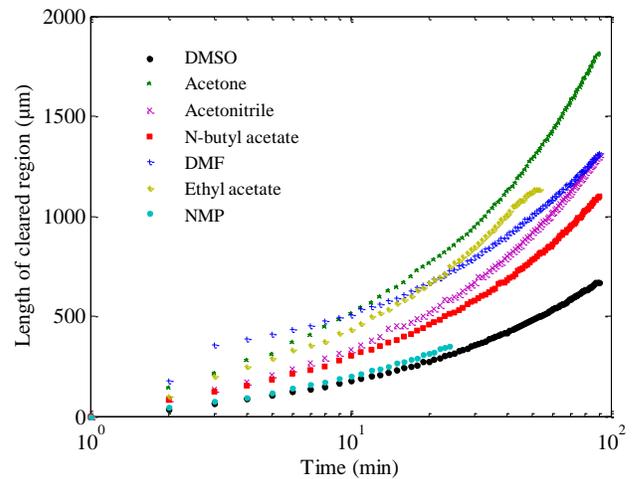


Figure 3: Dissolution data for dipolar aprotic solvents.

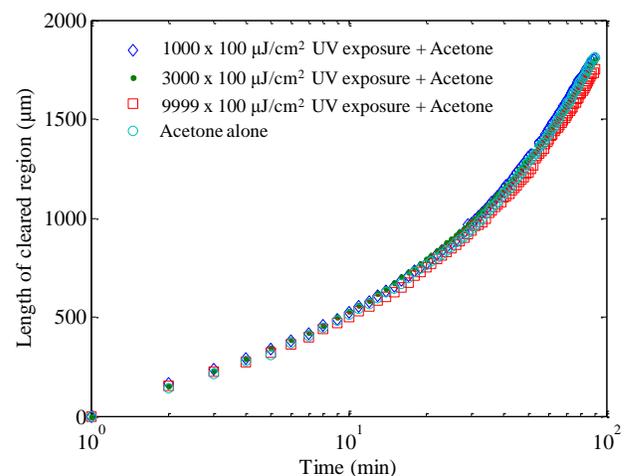


Figure 4: Dissolution data for different UV exposure values.

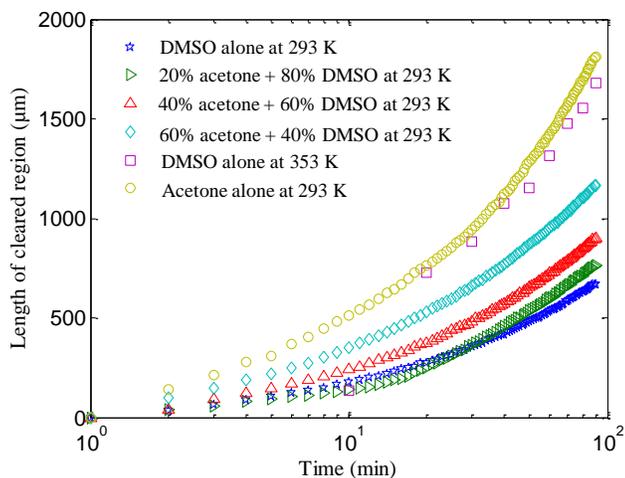


Figure 5: Dissolution data for DMSO at different temperatures and percentages [v/v] with acetone.

5 CONCLUSIONS

In conclusion, the dissolution of photo resist encapsulated in a microchannel was examined both theoretically and experimentally. The micro channels were fabricated by using standard micro fabrication processes. In the experiments, different types of solvents were used and the effects of different parameters, such as temperature on dissolution rate were examined. It was concluded that dipolar aprotic solvents could be used in the dissolution of photo resist inside the micro channels. Increasing the temperature increases the dissolution rate while UV exposure has almost no effect on the rate. Among the dipolar aprotic solvents, DMSO with its high boiling temperature and low evaporation rate, offers promise as an alternative to acetone to strip photo resist in the channels.

ACKNOWLEDGEMENT

The authors acknowledge the financial support of TUBITAK (The Scientific and Technological Research Council of Turkey) for Ph.D. Fellowship.

REFERENCES

- [1] M. G. Khan and A. Fartaj, "A review on microchannel heat exchangers and potential applications," *International Journal of Energy Research*, 35, 553-582, 2011.
- [2] A. Koyuncuoğlu, R. Jafari, T. Okutucu-Özyurt, and H. Külah, "Heat transfer and pressure drop experiments on CMOS compatible microchannel heat sinks for monolithic chip cooling applications," *International Journal of Thermal Sciences*, 56, 77-85, 2012.

- [3] K. Choi, J.-Y. Kim, J.-H. Ahn, J.-M. Choi, M. Im, and Y.-K. Choi, "Integration of field effect transistor-based biosensors with a digital microfluidic device for a lab-on-a-chip application," *Lab on a Chip*, 12, 1533-1539, 2012.
- [4] H. Ceylan Koydemir, H. Kulah, C. Ozgen, A. Alp, and G. Hascelik, "MEMS biosensors for detection of methicillin resistant *Staphylococcus aureus*," *Biosensors & Bioelectronics*, 29, 1-12, 2011.
- [5] J. P. Beech, S. H. Holm, K. Adolffson, and J. O. Tegenfeldt, "Sorting cells by size, shape and deformability," *Lab on a Chip*, 12, 1048-1051, 2012.
- [6] D. Huh, B. D. Matthews, A. Mammoto, M. Montoya-Zavala, H. Y. Hsin, and D. E. Ingber, "Reconstituting Organ-Level Lung Functions on a Chip," *Science*, 328, 1662-1668, 2010.
- [7] S. Sukas, A. E. Erson, C. Sert, and H. Kulah, "A parylene-based dual channel micro-electrophoresis system for rapid mutation detection via heteroduplex analysis," *Electrophoresis*, 29, 3752-3758, 2008.
- [8] E. Yildirim and H. Kulah, "Analysis and characterization of an electrostatically actuated in-plane parylene microvalve," *Journal of Micromechanics and Microengineering*, 21, 105009, 2011.
- [9] C. P. Tan and H. G. Craighead, "Surface Engineering and Patterning Using Parylene for Biological Applications," *Mater.*, 3, 1803-1832, 2010.
- [10] K. Walsh, J. Norville, and Y. C. Tai, "Photoresist as a sacrificial layer by dissolution in acetone," in *14th IEEE International Conference on Micro Electro Mechanical Systems, Technical Digest* 114-117, 2001.
- [11] M. Dahmardeh, W. Khalid, and M. S. Mohamed Ali, "High aspect ratio 3-D Micromachining of carbon-nanotube forests by micro-electro discharge machining in air", *MEMS 2011*, 272-275, 2011.