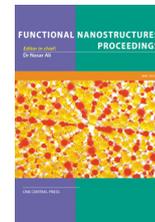


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# Further improvement of the unevenness of the edge portion of the coating film after drying by controlling the evaporation rate of the edge's side surface of the coating liquid film during drying

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## ABSTRACT

The drying of polymer solutions coated on a flat substrate is very important in various industrial applications such as fabricating flat polymer resist thin films in resist coating process in semiconductor process and so on. We have proposed and modified a model of the drying process of a polymer solution coated on a flat substrate for uniform polymer film deposition. In this study, in order to further reduce the thickening of the edge of the thin film after drying, we tried to adequately control the evaporation rate on the side of the liquid film at the edge. As a result, it was found that appropriate management of the evaporation rate on the side of the liquid film at the edge during drying further reduces the thickening at the edge after drying.

## I. INTRODUCTION

The drying of polymer solutions coated on a flat substrate is very important in various industrial applications such as fabricating flat polymer resist thin films in resist coating process in semiconductor process [1, 2] and so on. There are various studies of this process. Previous studies of the fabrication of flat polymer thin films have focused on the temporal variation in the thickness of polymer liquid films during drying [2, 3], without considering spatiotemporal variation in concentration distribution. Previous studies of inkjet printing have discussed drying of droplets of polymer solution [4, 5], and thus have a different scope from our study, which considers a large-area liquid film of polymer solution.

We have proposed and modified a model of the drying process of a polymer solution coated on a flat substrate for uniform polymer film deposition [6 - 11]. And we clarified the dependence of the distribution of polymer molecules on a flat substrate after drying on various parameters based on the analysis of many numerical simulations of the model.

However, the mechanism of the drying process in the previous studies does not allow problems with thin films after drying, such as thickening of the edges and depressions near the edge, to be avoided. We used the model to control the thickness of a thin film after drying through management of the temperature, evaporation, and concentration [12]. In addition, we applied the thermal, evaporative, and concentration management to the modified model incorporating the Marangoni effect [13]. As a result, we see that the thickening at the edge of the thin film after drying due to the Marangoni effect and so on can be improved through appropriate thermal, evaporative and solute concentration management.

However, on the other hand, it was also found that a certain degree of the thickening at the edge of the thin film after drying remained. In this study, in order to further reduce the thickening of the edge of the thin film after drying, we tried to adequately control the evaporation rate on the side of the liquid film at the edge. As a result, it was found that appropriate management of the evaporation rate on the side of the liquid film at the edge during drying further reduces the thickening at the edge after drying.

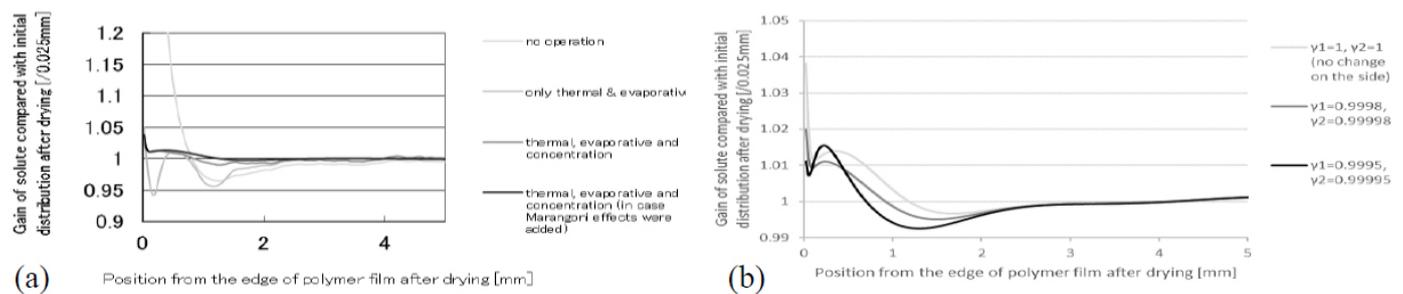
## II. METHOD OF THIS ANALYSIS

As a mathematical model, we use the following model which has been proposed by Kagami et al. [14].

$$\frac{\partial N}{\partial t} = K_C \nabla^2 N + \frac{N}{V} (K_V - K_C) \nabla^2 V - \frac{2K_C}{V} \nabla N \cdot \nabla V \quad (1)$$

where  $N$  denotes the number of solute molecules included in a space,  $K_C$  is the diffusion coefficient of the solution,  $V$  is the volume of solvent containing solutes included in a space and  $K_V$  is the diffusion coefficient of the solvent. Marangoni effect is incorporated into the model and treated the effect as pseudo-negative diffusion at an upper gas-liquid interface [15]. Then we control the vaporization rate and the concentration diffusion coefficient of the solution by managing the temperature, evaporation, and solute concentration of a solution film on the substrate. In particular, in this research, as mentioned above, we adequately control the evaporation rate on the side of the liquid film at the edge.

First, the results of the control of the thickening at the edge of the thin film after drying so far are shown below. The control is done as follows. If the integrated number of solute polymer molecules at a point on the substrate is more than (less than)  $\alpha_k$  times the initial average during drying, the temperature of the surface of the polymer solution film over the point is perturbed upward (downward) by  $\beta_k$ . In addition to raising or lowering the point temperature, if the integrated number of solute polymer molecules at a point on the substrate exceeds  $\alpha_k$  times the initial average during drying, the vaporization rate constant  $\gamma$  over the point is perturbed downward by  $\gamma_k$ . Furthermore, if the integrated number of solute polymer molecules at a point on the substrate exceeds  $\alpha_k$  times the initial average during drying, the solute concentration of the surface of the polymer solution film over the point is perturbed downward by  $\xi_k^{-1}$ . An example of the numerical simulation results is shown in Fig. 1(a) [13]. We can confirm reduction of the thickening of the edge of the thin film after drying.



**Figure 1** An example of the results of the control of the thickening at the edge of the thin film after drying by the numerical simulation of (a) the former model [13] and (b) the modified model.

## III. RESULTS AND DISCUSSION

In this trial, if the integrated number of solute polymer molecules at a point on the substrate is more than 1.1 or 1.02 times the initial average during drying, the vaporization rate constant  $\gamma$  at the upper surface over the point is perturbed downward by 0.9999 or 0.99999 and the vaporization rate constant  $\gamma$  on the side of the liquid film at the edge is perturbed downward by  $\gamma_1$  or  $\gamma_2$ . An example of the numerical simulation results is shown in Fig. 1(b). We can confirm further reduction of the thickening of the edge of the thin film after drying.

## IV. SUMMARY

In order to further reduce the thickening of the edge of the thin film after drying, we tried to adequately control the evaporation rate on the side of the liquid film at the edge. As a result, it was found that appropriate management of the evaporation rate on the side of the liquid film at the edge during drying further reduces the thickening at the edge after drying.

## V. REFERENCES

- [1] D. E. Bornside, C. W. Macosko and L. E. Scriven, "Spin coating: One-dimensional model," *J. Appl. Phys.*, vol. 66, pp. 5185-5193, 1989.
- [2] A. F. Routh and W. B. Russel, "Horizontal drying fronts during solvent evaporation from latex films", *AIChE J.*, vol. 44, pp. 2088-2098, 1998.
- [3] D. E. Bornside, C. W. Macosko and L. E. Scriven, "Spin coating: One-dimensional model", *J. Appl. Phys.*, vol.

- 66, pp. 5185-5193, 1989.
- [4] B. J. de Gans and U. S. Schubert, "Inkjet Printing of Well-Defined Polymer Dots and Arrays," *Langmuir*, vol. 20, pp. 7789-7793, 2004.
- [5] D. Soltman and V. Subramanian, "Inkjet-Printed Line Morphologies and Temperature Control of the Coffee Ring Effect," *Langmuir*, vol. 24, pp. 2224-2231, 2008.
- [6] H. Kagami, R. Miyagawa, A. Kawata, D. Nakashima, S. Kobayashi, T. Kitano, K. Takeshita, H. Kubota and T. Ohmi, "A model of coating and drying process for the flat polymer film fabrication," *Proc. SPIE.*, vol. 4754, pp. 252-259, 2002.
- [7] H. Kagami, "The influence of spatio-temporal variation of temperature distribution in a polymer solution on a flat substrate on formation of polymer film's thickness distribution during drying process - based on results of simulation of the modified model," *Proc. SPIE.*, vol. 5446, pp. 135-142, 2004.
- [8] H. Kagami, "A modified dynamical model of drying process of polymer blend solution coated on a flat substrate," *Proc. SPIE.*, vol. 7028, pp. 702825-1 - 9, 2008.
- [9] H. Kagami, "Characteristic three-dimensional structure of resist's distribution after drying a resist solution coated on a flat substrate: analysis using the extended dynamical model of the drying process," *Proc. SPIE.*, vol. 7273, pp. 727335-1 - 8, 2009.
- [10] H. Kagami, "A modified dynamical model of drying process of a polymer solution having plural solvents coated on a flat substrate for a flat and homogeneous polymer film fabrication," *Proc. SPIE.*, vol. 7716, pp. 771625-1 - 9, 2010.
- [11] H. Kagami and H. Kubota, "Applying the dynamical model of drying process of a polymer solution coated on a flat substrate to effects of bumpy substrate," *Proc. SPIE.*, vol. 7764, pp. 77640T-1 - 8, 2010.
- [12] H. Kagami, "More minute thickness control of a thin film after drying through temperature, evaporation and concentration management in drying process of a polymer solution coated on a flat substrate," *Proceedings of the 19th International Drying Symposium*, ISBN 978-2-7598-1631-6, 2014.
- [13] H. Kagami, "Control of the Marangoni Effect in the Drying Process of a Polymer Solution Coated on a Flat Substrate through Temperature Evaporation and Solute Concentration Management," *Athens Journal of Technology & Engineering*, Vol. 2, Issue 1, pp. 45-53, 2015.
- [14] H. Kagami, H. Kubota, "A dynamical model of drying process of a polymer solution having plural solvents and plural solutes (polymers) coated on a flat substrate for a flat and homogeneous polymer film fabrication," *Physica Status Solidi, C* 8, No. 2, pp. 586-588, 2011.
- [15] H. Kagami, "Impact of the Marangoni effect on the thin film thickness profile after drying polymer solution coated on a flat substrate," *JPS Conf. Proc.*, Vol. 1, pp. 015087-1 - 5, 2014.