ABSTRACT

The polymer resist coating process is important for precise semiconductor microfabrication, and a uniform polymer resist film thickness and homogeneous resist film quality are required. However, unevenness is observed on the resist film after drying. A cause of this unevenness is the non-uniform temperature in the device during drying. In this study, through numerical simulations we clarify the mechanism that explains why heating part of a polymer solution film on a substrate from the bottom produces a locally thicker film after drying, and the dependence of the unevenness of the film on the latent heat of vaporization. The larger the latent heat, the thicker the polymer resist film after drying in the heated region. This occurs because the temperature decrease caused by the latent heat of vaporization is recovered faster when the latent heat of vaporization is larger.

I. INTRODUCTION

The polymer resist coating process is important for precise semiconductor microfabrication and a uniform resist film thickness and homogeneous resist film quality are required [1, 2, 3, 4]. The resist films used in the semiconductor process are typically hundreds of nanometers thick, although the thickness depends on factors such as the purpose and the type of industry. The drying of the polymer resist solution coated on the substrate is crucial in the resist coating process.

We have proposed and modified a model for the drying process of polymer solutions coated on a flat substrate for uniform and homogeneous polymer film deposition and have clarified the mechanism of the drying process [5, 6, 7, 8, 9, 10, 11]. These models and the following discussion apply not just to nanoscale semiconductor processes, but also to general industrial processes.

Unevenness is observed on the resist film after drying. One cause of this unevenness is the non-uniform temperature in the device during drying; thus, we have clarified how the non-uniform temperature affects the film thickness distribution after drying through experiments and numerical simulations [12]. Therefore, temperature control of the coated polymer solution film during drying may eliminate the unevenness.

In this work, we investigate obtaining the desired film thickness distribution with no unevenness by temperature control of the coated polymer solution film during drying. We determine the vaporization latent heat dependence of locally thicker thin film formation by partial heating of a polymer solution film on the substrate from the bottom during drying, which is important for temperature control of the coated polymer solution film during drying. Through numerical simulations, we clarify the mechanism by which heating part of a polymer solution film on the substrate from the bottom produces a locally thicker polymer thin film after drying and the dependence of the unevenness of the film on the latent heat of vaporization. In addition, we verify the mechanism in a three-dimensional numerical simulation.

II. PREVIOUS EXPERIMENTAL RESULTS

First, we provide an overview of previous
experimental results [12]. An aqueous solution of Metolose, a polymer, was coated on a flat substrate and dried under reduced pressure in the device (Fig. 1(a)). The substrate was pinpoint heated from the bottom by a halogen lamp during drying. The thickness distribution of the thin film of Metolose formed on the substrate after drying is shown in Fig. 1(b). The position that was irradiated is shown by a light symbol below the X-axis.

The experimental results were verified by the numerical simulation of the model. Local circular heating from the bottom (Fig. 1(a)) was added to the polymer solution film in the numerical simulation. The numerical simulation results are shown in Fig. 1(c), where $N$ is the number density of polymer molecules in the central region after drying. Comparing Figs. 1(b) and 1(c) shows that the results of the numerical simulation reproduce the experimental results well.

Figure 1 (a) Schematic of the device in which the polymer solution is dried under reduced pressure [12]. (b) Thickness distribution of the Metolose thin film formed on the substrate after drying [12]. (c) Results of the numerical simulation of the model with local circular heating [12].

III. MODEL

The details of the theory and the basic equations have been reported in previous papers: [5, 7, 8, 9, 10]; thus, only the basic equations are shown here. First, we consider the following evaporation model.

\[ G = \gamma (1 - \beta C) \]  

where $G$ is the evaporation rate, $C$ is the concentration of the solution, and $\beta$ is a constant. Furthermore,

\[ \gamma = K \sqrt{\frac{M}{2\pi RT}} P_0 \]  

is a correction factor, where $P_0$ is the vapor pressure, $M$ is the molecular weight, $R$ is the gas constant, $T$ is temperature, and $K$ is a correction factor for the theoretical evaporation rate [13]. The two diffusion models are formulated as follows. First, the diffusion equation for solvent-containing solutes is written as

\[ \frac{\partial V}{\partial t} = K_v \nabla^2 V - \gamma (1 - \beta C) \]  

where $V$ is the volume of solvent-containing solutes included in a space and $K_v$ is the diffusion coefficient of the solvent. The second term on the right-hand side of Eq. (3) is solely for the interface between liquid and gas. The diffusion equation governing the change in concentration in solution is written as

\[ \frac{\partial N}{\partial t} = K_c \nabla^2 N + N \left( \frac{N}{V} (K_v - K_c) \nabla^2 V - \frac{2K_c}{V} \nabla N \cdot \nabla \right) \]  

where $N$ is the number of solute molecules in a space and $K_c$ is the diffusion coefficient of the solution. $K_c$ changes with time (solution concentration) as

\[ K_c = \frac{k_b T}{6\pi R \eta_0 \left[ [\eta] C + 1 \right]} \]  

where $k_b$ is the Boltzmann constant, $\eta_0$ is the viscosity of the solvent, and $[\eta]$ is the intrinsic viscosity. It is assumed that the vapor pressure of the solvent drops due to a drop in temperature, obeying the Clapeyron-Clausius equation as

\[ \frac{dP}{dT} = \frac{LP}{RT^2} \]  

where $P$ is vapor pressure, $R$ is the gas constant, and $L$ is the latent heat of the solvent [14, 15]. When the correction factor of the evaporation model is $\gamma$, and temperature of the solvent before vaporization is $T_0$, and those after vaporization are $\gamma T_0$ and $T_0$, respectively, we can write [14, 15] as follows.

\[ \gamma' = \frac{T_0}{T} \exp \left\{ -\frac{L}{R \left( \frac{1}{T_0} - \frac{1}{T} \right)} \right\} \]  

In a numerical simulation of the model, local circular heating is added to the solution on the substrate from the bottom (Fig. 1).

IV. RESULTS AND DISCUSSION

Previous results. In a previous paper, we examined the cause of the formation of a thicker film in the heated region of the substrate after drying based on numerical simulations of a model of a polymer solution drying on a flat substrate. Based on the numerical simulation results, we clarified the mechanism by which the characteristic thickness distribution of the dried film formed. Here, we describe the main previous results. Fig. 2(a) shows the results of the numerical simulation of the model after drying for larger $L$.

The distribution of the polymer solution concentration just before the drying is complete obtained by numerical simulation is shown in Fig. 2(b). The concentration of the polymer solution after drying is larger in the heated region than in the non-heated region and the difference in concentration is larger at the bottom because of the heating effect. The total volume of vaporized solvent after drying is
shown in Fig. 2(c), where $[\text{V}]$ is the average total volume of vaporized solvent in the central region after drying. Fig. 2(c) shows that the total volume of vaporized solvent after drying is larger in the heated region than in the unheated region because the solvent vaporizes more readily in the heated region, thereby increasing the diffusion of polymer molecules and solvents. Thus, the resist film is thicker in the heated region after drying.

**Figure 2** Results of the numerical simulation of the model with local circular heating. (a) Distribution of the number of polymer molecules. (b) Concentration distribution at each layer of the polymer liquid film just before drying is complete. (c) Total volume of vaporized solvent after drying. (d) Dependence of thickness profile of the polymer resist thin film after drying on latent heat.

**Dependence of film thickness on latent heat of vaporization in two dimensions.**
The dependence of the thickness profile of the polymer resist thin film after drying on latent heat of vaporization for two-dimensional local circular heating based on the numerical simulation is shown in Fig. 2(d). The larger the latent heat is, the thicker the polymer resist film after drying is in the heated region.

**Dependence of film thickness on latent heat of vaporization in three dimensions.**
Here, we show the dependence of the thickness profile of the polymer resist thin film after drying on the latent heat of vaporization for three-dimensional local circular heating based on the numerical simulation. Because it is difficult to compare two- and three-dimensional graphs, cross-sectional graphs are compared. The results of the three-dimensional numerical simulation of the model with local circular heating are similar to those of the two-dimensional simulation (Fig. 3(a)).
Figure 3 (a) Results of the three-dimensional numerical simulation of the model with local circular heating. (b) Dependence on the latent heat of vaporization of the thickness profile of the polymer resist thin film after drying for three-dimensional local circular heating based on the numerical simulation. The cross-sectional graphs are taken 0.25 mm from the heated edge.

Fig. 3(b) shows the dependence on the latent heat of vaporization of the thickness profile of the polymer resist thin film after drying for three-dimensional local circular heating based on numerical simulation. The cross-sectional graphs are taken 0.25 mm from the heated edge. The three-dimensional results are similar to those for two dimensions. Namely, the larger the latent heat is, the thicker the polymer resist film is in the heated region after drying. This is because the temperature decrease caused by the latent heat of vaporization recovers relatively more strongly when the latent heat of vaporization is larger.

V. SUMMARY

We examined the mechanism that explains why heating part of a polymer solution film on a substrate from the bottom produces a locally thicker polymer thin film after drying and the dependence of the unevenness of the film on the latent heat of vaporization in two- and three-dimensional numerical simulations. The larger the latent heat is, the thicker the polymer resist film after drying is at the heated region. This is because the temperature decrease caused by the latent heat of vaporization recovers relatively more strongly when the latent heat of vaporization is larger. Therefore, if a locally thicker thin film is desired, a solvent with a large latent heat of vaporization should be used.

VI. REFERENCES