

Session C-1

Core – Electronics Materials(1)

Polytetrafluoroethylene (PTFE) Polymer Films Prepared by Synchrotron Radiation (Invited)

Akira YOSHIDA, M. UCHIDA, E. MATSUMOTO, A. WAKAHARA, Toyohashi University of Technology, Japan

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Ik Tae IM, Iksan National College, Korea

Kwang Sun KIM, Korea University of Technology and Education, Korea

Jung Keun CHO, Korea DNS Co. Ltd., Korea

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Kazuaki SAWADA, Masao ENDO, Yoshiaki TADOKORO, Hidekuni TAKAO, Makoto ISHIDA, Toyohashi University of Technology, Japan

Shoji KAWAHITO, Shizuoka University, Japan

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Ik-Tae Im^a, Kwang-Sun Kim^b, and Jung Keun Cho^c

a) Dept. of Automotive Eng., Iksan National College
194-5 Ma-dong Iksan, 570-752 Korea

itim@iksan.ac.kr

b) Dept. of Mechatronics Eng., Korea Univ. of Tech. and Education
307 Gajeon-ri Byungchon-Myun Chonan, 330-708 Korea

kskim@kut.ac.kr

c) Korea DNS Co. Ltd.

623-5 Upsong-dong Chonan, 333-290 Korea

Abstract

Flow, mass transfer and film thickness variation during a thick photoresist film formation on a wafer spin coating process are numerically studied. Governing equations and boundary conditions for the cylindrical coordinates are simplified using the von Karman similarity transformation and solved by the finite difference method. The viscosity and binary diffusion coefficient are assumed to be functions of solvent concentration and the mass transfer coefficient is used to model the solvent evaporation from a free surface. The velocity components for the coating liquid and the film thickness variation with time are analyzed according to the various process parameters such as spin speeds and the initial photoresist concentrations. When the evaporation is considered, the velocity components are small due to the increase of viscosity and resultant decrease of outflow rate. The final film thickness is predicted from the wet film thickness, the thickness at the end of the spin coating process and the initial solute concentrations.

Introduction

There are an increasing number of researchers who are interested in the technologies that use thick photoresist films such as Micro-Electro-Mechanical Systems (MEMS) or Thin Film Heads (TFH). In conventional semiconductor applications such as IC, a photoresist film thickness of less than two microns is typically used and the film formation processes are relatively well known. But now with growing interest in the thick film technologies, the effects of process parameters during formation of a ultra-thick photoresist film are needed.

In some MEMS applications, film greater than twenty microns are frequently developed to produce mechanical structures such as channels, fins, and column array. For certain mechanical structures such as gears and pumps, the photoresist thickness requirements are easily exceed a hundred microns. The bump bond applications can also require photoresist film thickness in excess of a hundred microns. The thick photoresist film, about a hundred microns is used to define the location and size of the bump bond.

These thick films on a wafer surface are prepared using spin coating processes in general. The studies on the thin film spin coating process reveal that the film thickness is controlled by the two main film thinning mechanisms. In the early stage of the process, the flow out of the coating liquid to the radial direction due to the convection is a main film thinning

mechanism and is often called as spin-off stage. However, since the convective outflow continuously slows because of the film thickness decrease and the coating liquid viscosity rising, the evaporation becomes main film thinning mechanism. The fundamentals of flow and mass transfer during the spin coating process with mathematical models could be found in the work of Bornside *et al.*[1].

In this study, the centrifugal driven coating liquid flow and the mass transfer of solvent are modeled to analyze the thick photoresist film spin coating process. Von Karman similarity transformation on the equation of motion and the corresponding boundary conditions are used. The effect of evaporation is formulated into a parameter which form a free surface boundary condition. The dry film thickness is predicted from the simultaneous analysis of fluid flow and the evaporation. The fluid flow and the film thickness variation are examined according to the various coating liquid concentrations and spin speeds.

Mathematical Analysis

Consider the liquid film its axial thickness is very small compared to the radius on the circular disc. The disc rotates at the speed of $\Omega(t)$ and a coating liquid is a Newtonian fluid with constant density. Let (u, v, w) represent the velocity components for the cylindrical coordinates (r, θ, z) , the governing equations are the continuity and momentum and concentration transport equations. The following similarity and dimensionless variables are introduced.

$$u(r, z, t) = rf(z, t) \quad (1a)$$

$$v(r, z, t) = rg(z, t) \quad (1b)$$

$$w(r, z, t) = w(z, t) \quad (1c)$$

$$p(r, z, t) = -\frac{r^2}{2} \rho A(z, t) + \rho B(z, t) \quad (1d)$$

$$\tau = t\Omega_0, \quad \eta = z/h_0, \quad H = h/h_0,$$

$$F = f/\Omega_0, \quad G = g/\Omega_0, \quad W = w/h_0\Omega_0 \quad (2)$$

where h_0 and Ω_0 are the initial film thickness and spin speed. After obtaining governing equations and the boundary and initial conditions under the assumption of axisymmetric, applying the above variables gives the following equations.

$$\frac{\partial F}{\partial \tau} + F^2 - G^2 + W \frac{\partial F}{\partial \eta} = \frac{\partial}{\partial \eta} \left(Ek \frac{\partial F}{\partial \eta} \right) \quad (3)$$

$$\frac{\partial G}{\partial \tau} + 2FG + W \frac{\partial G}{\partial \eta} = \frac{\partial}{\partial \eta} \left(Ek \frac{\partial G}{\partial \eta} \right) \quad (4)$$

$$2F + \frac{\partial W}{\partial \eta} = 0 \quad (5)$$

$$\frac{\partial x}{\partial \tau} + W \frac{\partial x}{\partial \eta} = \frac{\partial}{\partial \eta} \left(Pe \frac{\partial x}{\partial \eta} \right) \quad (6)$$

where x is the solvent mass fraction, $Ek = \frac{v}{h_0^2 \Omega_0}$ is the

Eckman number, $Pe = D(x)/h_0^2 \Omega_0$ is the reciprocal of the Peclet number. Similarly, initial and boundary conditions are as follows.

$$F(\tau, 0) = 0, G(\tau, 0) = \Omega(\tau)/\Omega_0, W(\tau, 0) = 0 \quad (7a)$$

$$\frac{\partial F(\tau, H)}{\partial \eta} = \frac{\partial G(\tau, H)}{\partial \eta} = 0 \quad (7b)$$

$$\frac{\partial H}{\partial \tau} = W(\tau, H) - St(x_H - x_\infty) \quad (7c)$$

The boundary conditions for the mass transport are

$$\frac{\partial x(\tau, 0)}{\partial \eta} = 0 \quad (8a)$$

$$\frac{1}{1 - x_H} \frac{\partial x(\tau, H)}{\partial \eta} + Sh(x_H - x_\infty) = 0. \quad (8b)$$

Where $St = k/(h_0 \Omega_0)$ is the Stanton number, $Sh = kh_0/D$ is the Sherwood number, k is the mass transfer coefficient and D is the binary diffusivity. The initial solvent concentration is assumed to be uniform and the initial velocity profiles are determined from the continuity and momentum equations[1].

Numerical Method

Above equations (3)~(6) with boundary conditions can be solved efficiently by the finite difference method. As the film thickness is continuously decreasing with time, the conventional finite difference method cannot be used and the time dependent physical domain has to be transformed to a

fixed computational domain of (0,1). Following Dandapat and Layek[2], the transformation shown below is used.

$$\xi(\tau) = 1 - a_1 \ln \left[\frac{a_2 H(\tau) - \eta}{b_2 H(\tau) + \eta} \right], \quad 1 < c < \infty \quad (9)$$

Here $a_1 = \{\ln(a_2/b_2)\}^{-1}$, $a_2 = c+1$ and $b_2 = c-1$.

The parameter c controls the grid spacing in the physical domain. The fully implicit and the Crank-Nicholson scheme is used to discretize the transformed equations and the resultant algebraic equations are solved by the tri-diagonal matrix algorithm(TDMA). The F and G values are computed in each time level and then W is obtained from the finite difference representation of the equation (3). From the numerical test, the results of the fully implicit and the Crank-Nicholson method are completely coincident within the computational round-off errors. All computations are carried out on 51 grid points that is determined from the grid dependency test.

The concentration dependent viscosity model proposed by Meyerhofer[3] is used :

$$\mu = \mu_0(1 - x) + \mu_s \quad (10)$$

where $\mu_0 = 10\,000$ P and $\mu_s = 0.01$ P. The concentration dependent relationship for diffusivity proposed by Flack *et al.*[4] in their modeling study of spin coating process is used here.

$$D = D_0 \exp \left(\frac{x}{ax + b} \right) \quad (11)$$

Here $D_0 = 7.8 \times 10^{-12}$ cm²/s, $a = 0.04$ and $b = 0.043$. Following Sparrow and Gregg[5], the mass transfer coefficient is

$$k = 4 \times 10^{-5} \sqrt{\Omega}. \quad (12)$$

Results and Discussion

Solvent evaporation is a film thinning mechanism itself and has influence on the flow through the materials properties of the coating liquid. Results from the analysis of considering solvent evaporation and without evaporation by setting $k = 0$ are compared in Fig. 1, 2 and 3. Fig. 1 shows the film thickness variation according to time. The liquid film thickness decrease rapidly in the early times and most of film thinning is accomplished in a few seconds. When the evaporation is not included in the analysis, depicted as a dashed line, the film thinning rate is greater than the solid line. This is due to the coating fluid viscosity rise as solvent evaporates. If the solvent evaporation is not included, the viscosity is a constant and is very small compared to that of including solvent evaporation. It is shown in figure 2 and 3 that the magnitude of the velocity is small in the case of considering evaporation. Both of the magnitude of radial velocity, F and axial velocity, W are small when evaporation is considered. It is clear that the rate of liquid depletion from the disc is smaller if the evaporation is included. This is due to the fact that the increased viscosity resulted from solvent removal produces a greater resistance to the fluid flow.

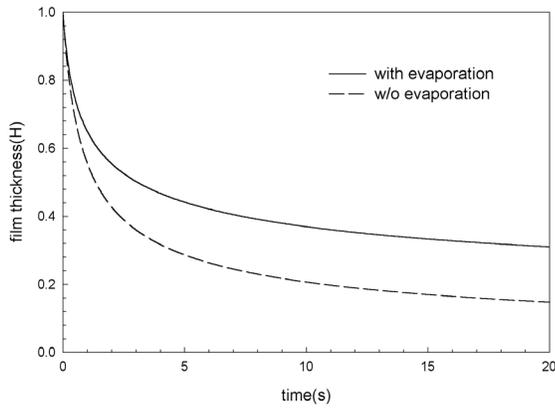


Fig. 1 Film thickness variations with time at spin speed of 2000 rpm.

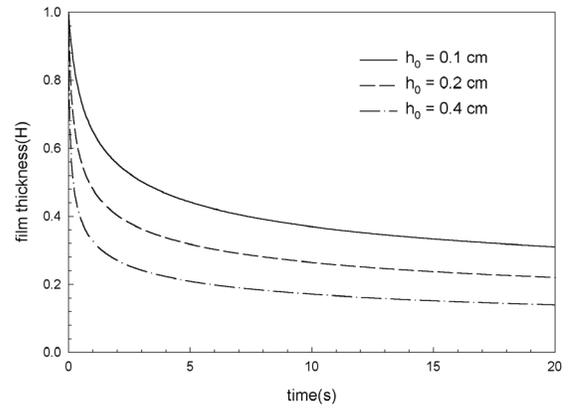


Fig. 4 Variation of the film height H with time for different initial thickness, $\Omega = 2000$ rpm and $x_i = 0.6$.

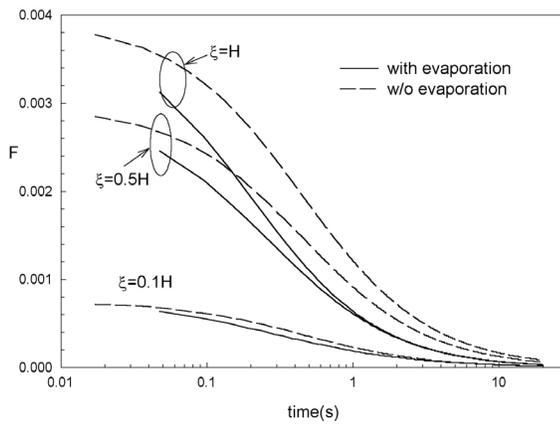


Fig. 2 Time variations of the radial velocity F at different film height for spin speed 2000 rpm, $x_i = 0.6$ and $x_\infty = 0.0$.

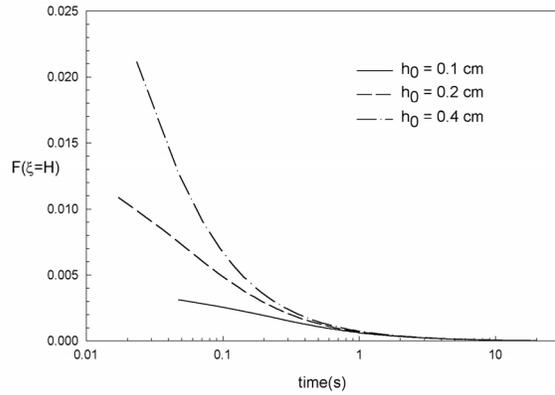


Fig. 5 Variations of the radial velocity F with time at the film surface for different spin speeds.

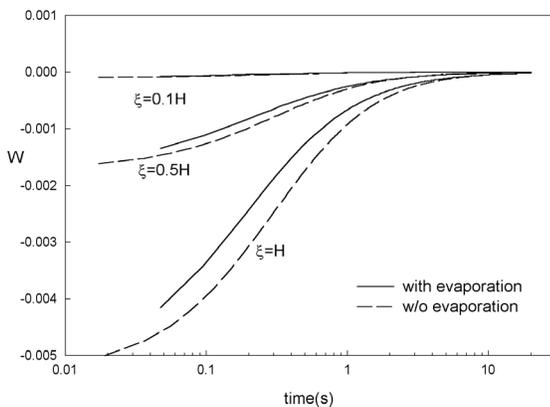


Fig. 3 Time variations of the axial velocity W at different film height for spin speed 2000 rpm, $x_i = 0.6$ and $x_\infty = 0.0$.

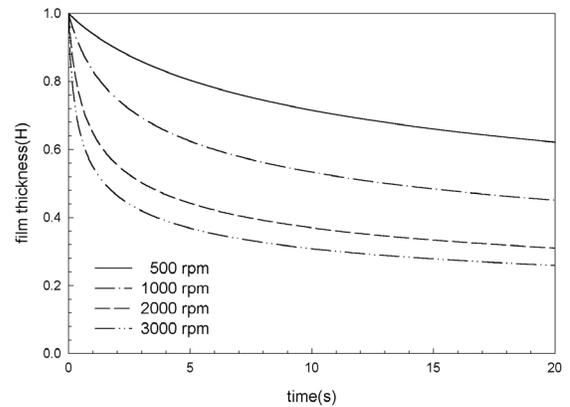


Fig. 6 Variation of the film height H with time for different rotation speeds, initial film thickness and solvent mass fraction are 0.1 cm and 0.6, respectively.

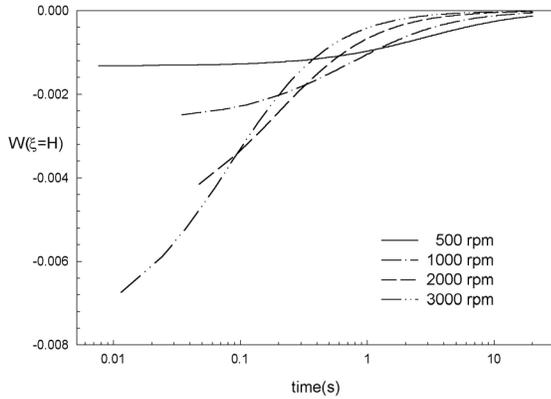


Fig. 7 Variation of the axial velocity W at film surface with time for different rotation speeds, the process conditions are the same as figure 6.

Fig. 4 shows the time variations of film thickness according to the initial dispensed film thickness, h_0 . The wafer spin speed is 2000 rpm and the initial solvent mass fraction $x_i = 0.6$. The film thinning rate is greater as the initial film is thicker. This is due to the fact that the flow rates to the radial and axial directions and the inertial forces become larger as film becomes thicker. The radial velocities F at the free surface for the various initial film thicknesses are shown in Fig. 5. This shows that the rate of flow out from the disc becomes greater as initial film thickness h_0 grows. It is interesting that after about a second, the F values are similar and therefore the amount of flow out becomes equal regardless of the initial film thickness. It means that thick film thins very rapidly and this fact agrees with the analytical result that the rate of film thinning by convective out flow is proportional to film thickness cubed[6].

Fig. 6 represents the variation of film thickness with time at different spin speeds for $x_i = 0.6$ and $h_0 = 0.1$ cm. The film thinning rate becomes greater as the spin speed becomes high, as expected. The variations of axial velocity at the film surface with time are shown in Fig. 7. The magnitude of velocity at high spin speed shows rapid decrease due to the decrease of film thickness. It is shown that after about a second, velocities for lower spin speeds becomes greater than higher spin speeds at the film surface.

Conclusions

A spin coating process for obtaining a thick photoresist film is numerically analyzed in this study. Flow of a coating liquid and evaporation are modeled by the von Karman similarity transformations. Concentration dependent viscosity and diffusivity are introduced. Fluid flow disappears more rapidly when the evaporation effect is included in the analysis due to the viscosity increase. Film thinning rate becomes larger as the initial film thickness becomes thick and the rotation speeds are high.

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