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# Mathematical analysis of soft baking in photolithography

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(Received 21 February 2000; accepted for publication 1 November 2000)

The soft baking step of a photolithography process is analyzed theoretically, taking the effect of the temperature dependence of the diffusivity of solvent into account. A coordinates-transform technique is chosen to solve the moving boundary problem under consideration. The temporal variation of the thickness of a film is predicted, and the result obtained justified by fitting experimental data reported in the literature for both poly(methylmethacrylate) film and Shipley UVIII photoresist. We show that, depending upon the types of photoresist film and the operating conditions, the transport of solvent may be controlled by the diffusion of solvent in a film or the convective transport of solvent from the gas–film interface to the bulk gas phase. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1335823]

## I. INTRODUCTION

The lithographic process is one of the most important processes for microelectronic fabrication.[1] Various patterns on a silicon wafer are formed through exposing and developing steps of a photoresist. The diffusion ability of a photoactive compound contained in a photoresist film plays an important role on the photochemical reaction in a lithographic process.[2–5] Therefore, the control of the free volume inside a photoresist film before its exposure to a light source significantly influence the quality of the lithography process. The adhesion of a photoresist film to substrate is also found to be affected by its solvent content. In practice, the free volume (or solvent content) of a spin-coated photoresist film can be controlled by appropriately selecting the basic parameters, such as, baking temperature and baking time of a soft baking process. Apparently, a detailed understanding of the soft baking mechanism is essential to a lithographic process.

Intuitively, three mechanisms are involved in a soft baking process: the diffusion of solvent to film–gas interface, the evaporation of solvent, and the subsequent transport of solvent vapor to the bulk gas phase. This implies that the essential physical parameters that relate to a soft baking process are the diffusivity of solvent in photoresist film, the mass transfer coefficient of solvent at the film–gas interface, the baking temperature, and baking time. The significant role played by soft baking has stimulated several interesting and important studies.[6–13] Batchelder and Piatt, for example, revealed the importance of baking effects of positive photoresists.[6] They found that a very high soft baking temperature leads to a low dissolution rate of photoresist and thus reduces the production rate of microelectronics. On the other hand, a low soft baking temperature yields high solvent retention, and adhesion failure occurs to a photoresist film. Paniez *et al.*[7] proposed a relaxation time model for the temporal variation of photoresist thickness during soft baking. A linear relation between the thickness and the logarithm of time was obtained. Paniez and co-workers later used the experimental techniques of contact angle measurement[8] and real-time *in situ* ellipsometry[10] to study the soft baking mechanism. They found that the soft baking procedure is affected by the glass transition temperature of polymer and the hydrogen bonding of solvent. Pain *et al.*[10] found that the related delay-time effects such as contamination and critical dimension variations could be markedly reduced by an appropriate selection of soft baking conditions. Mack *et al.*[11] proposed a diffusion-controlled model to describe the solvent distribution and resist thickness after soft baking. In this model, the diffusivity was assumed to be dependent on solvent concentration; some discrepancy between the experimental data and simulated results was observed. In a recent study Lin *et al.*[13] conducted a theoretical analysis of the soft baking procedure. The significance of the convective transport of solvent from film–gas interface to the bulk gas phase was discussed, and a lumped model describing the temporal variation of film thickness was derived.[13]

Although experimental results for the soft baking process are ample in the literature theoretical investigations are relatively limited. In particular, a general model, which is capable of taking all the possible mechanisms of the process into account, has not been reported. In the present study, the lumped model of Lin *et al.*[13] is extended to take the effect of the temperature dependence of solvent diffusivity into account. The partial differential equation, which describes the temporal variation of spatial solvent concentration in a photoresist film, coupled with a moving boundary condition is solved analytically. The temporal variation of film thickness is estimated. The applicability of the result derived is justified by fitting the available experimental data for poly(meth-

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ylmethacrylate) (PMMA) film and Shipley UVIII photoresist film in the literature.

## II. MODELING

Figure 1 illustrates schematically the soft baking process under consideration. $L_{fi}$ and $L_p$ are the initial thickness of a photoresist film and the thickness of the corresponding solvent-free film, respectively. The solvent in the film is driven out in the $z$ direction by hotplate heating at the bottom of the wafer, and nitrogen gas blowing parallel to the film–gas interface. The thickness of the film at time $t$ is defined as $L_f(t)$. Due to the variation in the solvent content in the film, the location of the film–gas interface varies with time. Since solving the moving boundary problem directly is nontrivial, a coordinate transformation[14,15] is conducted so that it reduces to a fixed boundary problem. A schematic representation of the problem represented in $\xi$ coordinate is illustrated in Fig. 1(b). In the transformed coordinate, the amount of polymer contained in a unit length of $\xi$ is constant, and the thickness of the photoresist film $L_p$ is independent of time. For convenience, solvent is represented by $A$, and polymer by $B$. A mass balance on the amount of $A$ contained in the interval $\xi$ to $\xi+d\xi$ yields

$$\left[n_A-\left(n_A+\frac{\partial n_A}{\partial \xi}d\xi\right)\right]A_c=\frac{\partial \rho_A}{\partial t}A_c d\xi, \tag{1}$$

where $n_A$ and $\rho_A$ are the mass flux and the mass concentration of $A$, respectively, and $A_c$ is the cross-sectional area of the film. Equation (1) leads to

$$\frac{\partial \rho_A}{\partial t}=-\frac{\partial n_A}{\partial \xi}. \tag{2}$$

The mass flux of $A$ can be expressed as

$$n_A=-\rho D_A^B\frac{\partial x_A}{\partial \xi}, \tag{3}$$

where $\rho$, $x_A$, and $D_A^B$ are the mass concentration of the solvent–polymer mixture, the mass fraction of $A$, and the diffusivity of $A$ in $B$ defined in $\xi$ coordinate, respectively. Equations (2) and (3) lead to

$$\frac{\partial \rho_A}{\partial t}=-\frac{\partial}{\partial \xi}\left(-\rho D_A^B\frac{\partial x_A}{\partial \xi}\right)=\frac{\partial}{\partial \xi}\left(\rho D_A^B\frac{\partial x_A}{\partial \xi}\right). \tag{4}$$

At a constant baking temperature, the diffusivity of $A$ in $B$ is a function of free volume only, which is also the function of the volume fraction of $B$.[16] In reality, $D_A^B$ is highly dependent upon solvent content. In order to simplify the solution, however, we assume that it is constant. That is, $D_A^B=D$, which is $\xi$ independent. Also, since the solvent content in a photoresist film after spin-coating is usually limited, $\rho$ can be approximated by a constant. In this case Eq. (4) can be approximate by

$$\frac{\partial x_A}{\partial t}=D\frac{\partial^2 x_A}{\partial \xi^2}. \tag{5}$$

The initial and boundary conditions associated with this equation are

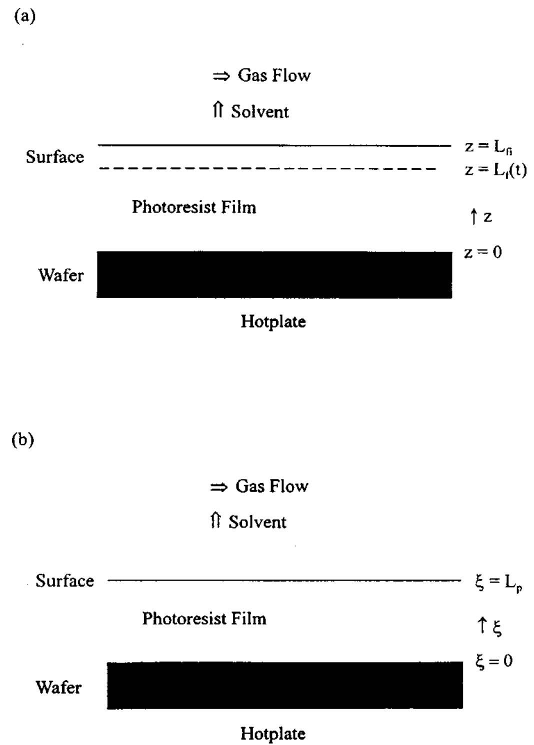


FIG. 1. (a) Schematic representation of the problem considered. Solvent diffuses in the $z$ direction and leaves the film–gas interface through evaporation and convection. $L_f(t)$, $L_{fi}$, and $L_p$ are film thickness at time $t$, initial film thickness, and solvent-free film thickness, respectively. (b) Transformed coordinates used in the mathematical analysis. The film–gas interface is fixed at $\xi=L_p$.

$$x_A(\xi,0)=x_{Ai}, \tag{5a}$$

$$\frac{\partial x_A(0,t)}{\partial \xi}=0, \tag{5b}$$

$$-D\frac{\partial x_A(L_p,t)}{\partial \xi}=k_m x_A(L_p,t), \tag{5c}$$

where $k_m$ is the mass transfer coefficient for the transport of $A$ from the film–gas interface to the bulk gas phase. Equation (5a) implies that the initial concentration of $A$ is uniform and is denoted as $x_{Ai}$, which can be expressed as

$$x_{Ai}=\frac{A_c(L_{fi}-L_p)\rho_s}{A_c(L_{fi}-L_p)\rho_s+A_cL_p\rho_p}=\frac{(L_{fi}-L_p)\rho_s}{(L_{fi}-L_p)\rho_s+L_p\rho_p}, \tag{5d}$$

where $\rho_s$ and $\rho_p$ are the densities of pure $A$ and pure $B$, respectively. Equation (5b) suggests that the wafer–film interface is impermeable to $A$. Equation (5c) states that, at the film–gas interface, the rate of transport of $A$ in the film is balanced by that to the bulk gas phase. For the high flow rate of gas flow, the solvent amount in the gas flow is usually tiny, and we make a good assumption of zero solvent content in the gas flow. Solving Eq. (5) subject to Eqs. (5a)–(5d) yields the spatial variation in the mass fraction of $A$. We obtain

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$$x_A(\xi^*,\tau)=2x_{Ai}\sum_{m=1}^{\infty}\left[\frac{S}{(\beta_m^2+S^2+S)\cos(\beta_m)}\cos(\beta_m\xi^*)\times\exp(-\beta_m^2\tau)\right], \tag{6}$$

where the scaled symbols are defined by $\xi^*=\xi/L_p$, $\tau=Dt/L_p^2$, and

$$S=\frac{k_m}{D/L_p}, \tag{6a}$$

and $\beta_m$ is the positive root of the equation

$$-\beta_m\sin(\beta_m)+S\cdot\cos(\beta_m)=0. \tag{6b}$$

The rate of decrease in the solvent content in a film can be described by

$$-\frac{dW_t}{dt}=-\frac{dW_s}{dt}=-\frac{d}{dt}[\rho_sA_c(L_f-L_p)]=-\rho_sA_c\frac{dL_f}{dt}=-\rho A_cD\frac{\partial x_A(L_p,t)}{\partial\xi}, \tag{7}$$

or

$$\frac{dL_f}{dt}=D\frac{\rho}{\rho_s}\frac{\partial x_A(L_p,t)}{\partial\xi}. \tag{8}$$

Equations (6) and (8) lead to

$$\frac{dL_f^*}{d\tau}=\frac{\rho}{\rho_s}\frac{\partial x_A(1,\tau)}{\partial\xi^*}=-\frac{2x_{Ai}\rho}{\rho_s}\sum_{m=1}^{\infty}\left[\frac{S^2}{\beta_m^2+S^2+S}\exp(-\beta_m^2\tau)\right]. \tag{9}$$

Integrating this expression gives the temporal variation of film thickness. We have

$$L_f^*=L_{\rm fi}^*-\frac{2x_{Ai}\rho}{\rho_s}\sum_{m=1}^{\infty}\left\{\frac{S^2}{\beta_m^2+S^2+S}[1-\exp(-\beta_m^2\tau)]\right\}. \tag{10}$$

### Limiting cases

Two limiting cases deserve further investigation. The Sherwood number $S$ is a measure of the relative significance of the rate of transport of $A$ through convection and that through molecular diffusion. Suppose that $S$ is large, that is, the transport of solvent in photoresist film is the rate-controlling step. This occurs, for example, if the rate of gas flow is high. In this case Eqs. (6) and (10) can be simplified, respectively, to

$$x_A(\xi^*,\tau)=2x_{Ai}\sum_{m=1}^{\infty}\left\{\frac{(-1)^{m-1}}{(m-1/2)\pi}\cos[(m-1/2)\pi\xi^*]\{1-\exp[-(m-1/2)^2\pi^2]\}\right\}, \tag{11}$$

and

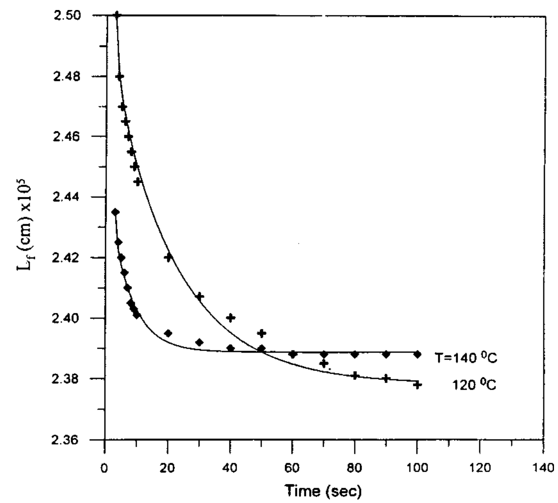


FIG. 2. Temporal variation in the film thickness of a PMMA film at various soft baking temperatures (Ref. 9). +: 120 °C, ◆: 140 °C. Solid lines are the results based on the present model. The parameters used are $\rho_s=0.944$ g/cm$^3$, $\rho_p=1.188$ g/cm$^3$. $L_p=237.3\times10^{-7}$ cm for 120 °C, and $238.8\times10^{-7}$ cm for 140 °C, respectively.

$$L_f^*=L_{\rm fi}^*-\frac{2x_{Ai}\rho_p}{\rho_s}\sum_{m=1}^{\infty}\left\{\frac{1}{(m-1/2)^2\pi^2}\times[1-\exp[-(m-1/2)^2\pi^2]]\right\}. \tag{12}$$

Consider, next, the other limiting case where $S$ is small. This occurs, for instance, if the soft baking temperature is high which results in a high diffusion rate and the transport of solvent through gas film becomes the controlling step. In this case the distribution of solvent in a film is uniform approximately, and $x_A=x_A(t)$. Equations (5c) and (7) lead to

$$\frac{dL_f}{dt}=-\frac{\rho}{\rho_s}k_mx_A(t). \tag{13}$$

We have

$$x_A=\frac{A_c(L_f-L_p)\rho_s}{A_c(L_f-L_p)\rho_s+A_cL_p\rho_p}=\frac{\rho_sL_f-\rho_sL_p}{\rho_sL_f+(\rho_p-\rho_s)L_p}. \tag{14}$$

Substituting this expression into Eq. (13) and integrating the resultant expression, we obtain

$$\frac{\rho_s}{\rho}(L_{\rm fi}-L_f)+\frac{\rho_pL_p}{\rho}\ln\left(\frac{L_{\rm fi}-L_p}{L_f-L_p}\right)=k_mt. \tag{15}$$

A similar expression was derived by Lin *et al.*[13]

## III. RESULTS AND DISCUSSIONS

The applicability of the model derived is justified by fitting the experimental data reported by Paniez *et al.*[9] for PMMA film and Shipley UVIII photoresist. Their data and the results evaluated by the present model are shown in Figs. 2 and 3. As can be seen from these figures, the performance of the present model is satisfactory, though not perfect.

In the data fitting procedure, the thickness of a solvent-free film, $L_p$, needs to be estimated in the first place. For a

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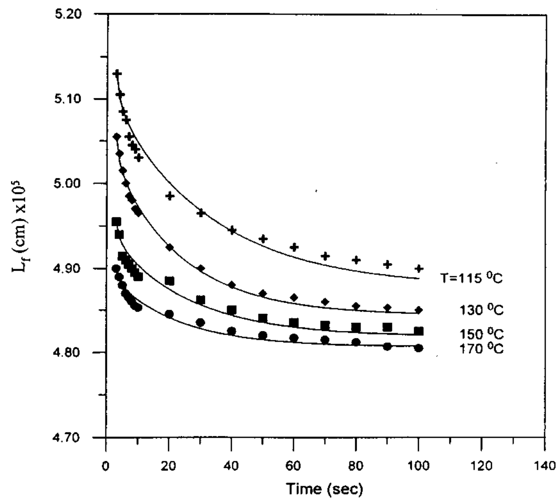


FIG. 3. Temporal variation of the thickness of Shipley UVIII photoresist film at various temperatures (Ref. 9). +: 115 °C, ♦: 130 °C, ■: 150 °C, ●: 170 °C. Solid lines are the results based on the present model. The parameters used are $\rho_s = 1.0\,\text{g/cm}^3$, $\rho_p = 1.1\,\text{g/cm}^3$. $L_p = 486.5\times10^{-7}$ cm for 115 °C, $483.5\times10^{-7}$ cm for 130 °C, $481.5\times10^{-7}$ cm for 150 °C, and $480.5\times10^{-7}$ cm for 170 °C, respectively.

PMMA film, its thickness usually approaches a constant value after a long operating time. This value can be used as an estimate for $L_p$. For Shipley UVIII films, however, two types of densification may occur. The first type of densification is mainly due to the decrease in its solvent content through evaporation. If the operating temperature exceeds the glass transition temperature of a film, its thickness various continuously even if the solvent is evaporated completely due to the second type of densification.[9] It is mainly due to the thermal deprotection of polymer material. The evaporation of protecting molecules of a film yields the increase in its free volume, which in turn leads to the second type of densification. In this case the $L_p$ of a film can be estimated by its thickness at which the second type of densification occurs.

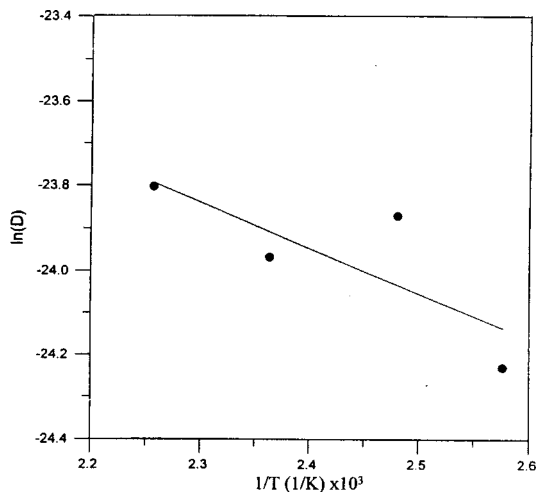


FIG. 4. Variation of logarithmic solvent diffusivity as a function of inverse temperature for Shipley UVIII photoresist film for the case of Fig. 3. The value of the activation energy obtained by linearly regression is $E_a = 8.9$ KJ/mole.

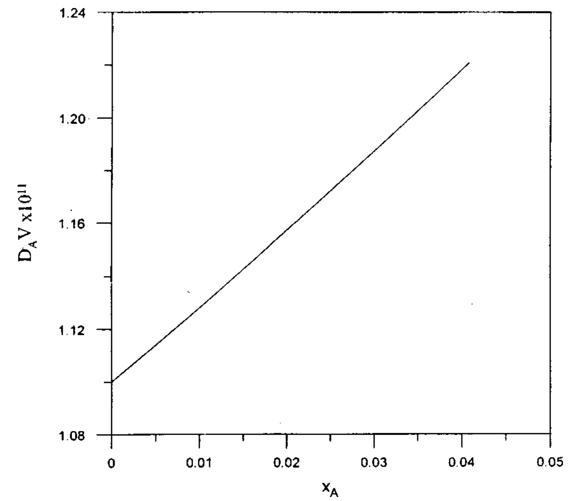


FIG. 5. Variation of solvent diffusivity in $z$ coordinate as a function of the weight fraction of solvent. The data of Fig. 2 at 120 °C are used.

Figure 4 summarizes the variation of ln($D$) as a function of $(1/T)$ for the results shown in Figs. 2 and 3. This figure suggests that the temperature dependence of $D$ follows the Arrhenius relation, that is, $D = A_r \exp(-E_a/RT)$, $E_a$ and $R$ being, respectively, the activation energy and the gas constant, and $A_r$ is a constant. The estimated activation energy is 8.9 KJ/mole, the order of magnitude of which is consistent with that of Dammel *et al.*[17] The diffusivity of solvent represented in $z$ coordinate, $D_A^V$, can by expressed as[15]

$$D_A^V = \frac{D_A^B}{(1-v_A)^2}, \tag{16}$$

where

$$v_A = \frac{x_A/\rho_s}{x_A/\rho_s + (1-x_A)/\rho_p} = \frac{x_A \rho_p}{(\rho_p - \rho_s)x_A + \rho_s}. \tag{17}$$

Equations (16) and (17) lead to

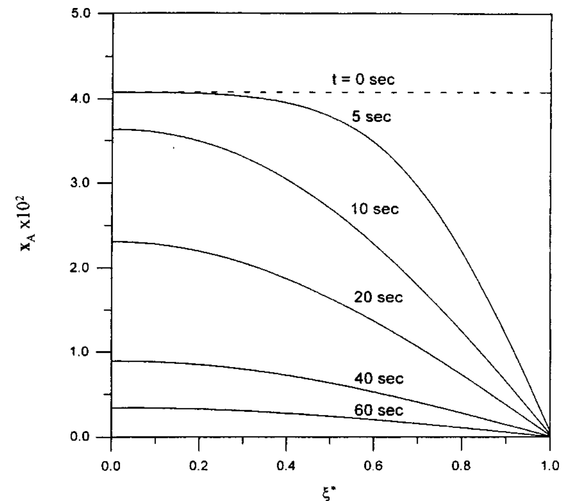


FIG. 6. Variation in the spatial variation in the mass fraction of solvent in the PMMA film of Fig. 2 at 120 °C and at various times.

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TABLE I. The fitted values of the adjustable parameters for PMMA film and Shipley UVIII photoresist at various soft baking temperatures.

| Type of film | Temperature (°C) | $D$ (cm$^2$/s) | $k_m$ (cm/s) | $S$ |
|---|---|---|---|---|
| PMMA | 120 | $1.1\times10^{-11}$ | $8.5\times10^{-5}$ | 183 |
| | 140 | $3.4\times10^{-11}$ | $1.1\times10^{-4}$ | 77 |
| Shipley UVIII | 115 | $3.0\times10^{-11}$ | $6.4\times10^{-5}$ | 104 |
| | 130 | $4.3\times10^{-11}$ | $6.1\times10^{-5}$ | 72 |
| | 150 | $3.9\times10^{-11}$ | $6.5\times10^{-5}$ | 80 |
| | 170 | $4.6\times10^{-11}$ | $5.9\times10^{-5}$ | 62 |

$$D_A^V=\left[\frac{(\rho_p-\rho_s)x_A+\rho_s}{-\rho_s x_A+\rho_s}\right]^2\cdot D_A^B. \tag{18}$$

Figure 5 illustrates the variation of $D_A^V$ as a function of $x_A$. This figure reveals that in the range $0<x_A<0.05$ using an averaged $D_A^V$ is appropriate.

Figure 6 shows the spatial variation in the mass fraction of solvent in the PMMA film of Fig. 2 at various times. This figure reveals that the distribution of solvent in a film is nonhomogeneous. The knowledge about the distribution of solvent in a film is of practical significance in photolithography. This is because the distribution of photoacid generator in a film before exposure can be known, and the distribution of free volume after exposure can also be estimated.[15] The latter can be used to control the diffusion of photogenerated acid in a photoresist,[18] which is essential to the performance of lithography.

Table I summarizes the fitted values of the adjustable parameters. According to this table, since $S$ is large under the experimental conditions chosen, the transport of solvent for both PMMA film and Shipley UVIII photoresist tends to be controlled by the diffusion of solvent. Table I also suggests that $k_m$ is independent of temperature for the experimental conditions examined.

## IV. CONCLUSION

In summary, a theoretical model for the description of the soft baking step of photolithography is derived, and is justified by fitting the experimental data for both PMMA film and Shipley UVIII photoresist. The rate of removal of solvent is found to be controlled by its diffusion in a film, and an Arrhenius type of relation exists between the diffusivity of solvent and temperature. The result predicted by the present analysis provides necessary information for the assessment of the performance of a photoresist film in photolithography.

## ACKNOWLEDGMENT

This work is supported by the National Science Council of the Republic of China.


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