JVSTB Journal of Vacuum Science & Technology B

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Wenan Loong and Hongtsz Pan

Citation: Journal of Vacuum Science & Technology B **8**, 1731 (1990); doi: 10.1116/1.585148
View online: http://dx.doi.org/10.1116/1.585148
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvstb/8/6?ver=pdfcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

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A direct approach to the modeling of polydihexylsilane as a contrast enhancement material

Wen-an Loong and Hong-tsz Pan
Institute of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China

(Received 29 May 1990; accepted 25 July 1990)

In our study the polydihexylsilane(PDHS), as a contrast enhancement material, we found that the values of *A*, *B*, and *C* of Dill's modeling parameters of PDHS are irregularly dependent on its film thickness, and also refractive index decreases during exposure. These difficulties make Dill's model inadequate for the simulation of contrast enhanced lithography. A new model was derived to simulate the nonlinear photobleaching curves of PDHS with varying thickness. Linearity was found with parameters in this equation as a function of PDHS film thickness. The thicker PDHS film does not improve the contrast within the usually used thickness range of 0.1–0.6 μm. This equation also models the nonlinear bleaching curve of *p*-diazo-*N*,*N*-dimethylaniline-chloride zinc chloride and the reported bleaching curve of CEM-2 quite well.

I. INTRODUCTION

Dill's modeling parameters,[1] namely, *A*, *B*, and *C* are generally used for the modeling and profile simulation of contrast enhanced lithography (CEL).[2–4] In our study of polydihexylsilane (PDHS) as a contrast enhancement material (CEM),[5] it was found that the measured values of *A*, *B*, and *C* of PDHS thin film bleaching curves were irregularly dependent on its thickness. This is contrary to the diazo-novolac based positive photoresists whose *A*, *B*, *C* values are independent of their thickness. In addition, the refractive index of PDHS thin film was found to decrease during exposure. Therefore, difficulties result when attempting to model the behavior of CEL by using Dill's parameters. Although Babu and Barouch[6,7] have reported the exact solutions for exposure bleaching of nonlinear resist material, it is still very difficult to apply to simulations of CEL. A direct approach was used in this paper to solve these difficulties. An equation with four parameters was derived to do the CEL modeling of PDHS. The PROLITH program[3] was modified to perform the sidewall profile simulations along with this equation. This equation can fit the reported data of CEM-2 (other name of CEM-388) very well. This equation can also simulate the nonlinear bleaching resist material of *p*-diazo-*N*,*N*-dimethylaniline chloride zinc chloride quite well.

II. EXPERIMENTAL

The PDHS was prepared as follows. The Grignard reagent of *n*-hexylmagnesiumbromide was formed by the reaction of *n*-hexylbromide and magnesium powder in dry ether, then, by titration, two moles of this freshly prepared Grignard reagent was reacted with one mole of tetrachlorosilane in *n*-heptane to form the di-*n*-hexyldichlorosilane. PDHS was prepared by sodium mediated Wurtz coupling of di-*n*-hexyl dichlorosilane. PDHS has an average Mw of 66 000 (by GPC, relative to polystyrene). *p*-diazo-*N*,*N*-dimethylaniline chloride zinc chloride is obtained from Tokyo Kasei. Bleaching measurements were performed by using an Oriel 500 W deep UV illuminator equipped with an Oriel 365 nm narrow band interference filter. The apparatus is similar to Ref. 4. PDHS was spincoated on a thin quartz plate which was not treated to match the refractive index of PDHS. Film thickness measurements were made with a Dektak IIA profilometer. The refractive index of PDHS thin film was taken using a Rudolph EL-III automatic ellipsometer.

III. RESULTS AND DISCUSSION

The measured Dill's values of *A*, *B*, and *C* of PDHS thin film spincoated on quartz plate are shown in Fig. 1 and indicate that their values are irregularly dependent on its thickness. The nonlinear photobleaching curves of PDHS with different thicknesses are shown in Fig. 2, from which the Dill's values are measured. The sampling time is 0.5 second in Fig. 2 and the bleaching curves are continuous lines. For the purpose of clarity and comparison with simulated values, only a few data points are shown for each of the five bleaching curves in Fig. 2. The refractive index of PDHS

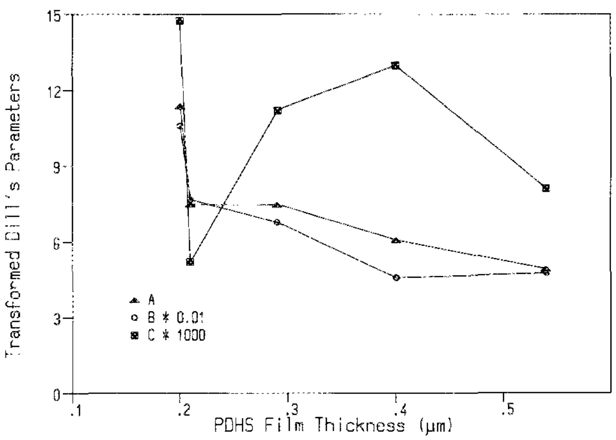

FIG. 1. Measured Dill's parameters *A*,*B*,*C* are irregularly dependent on PDHS film thickness.

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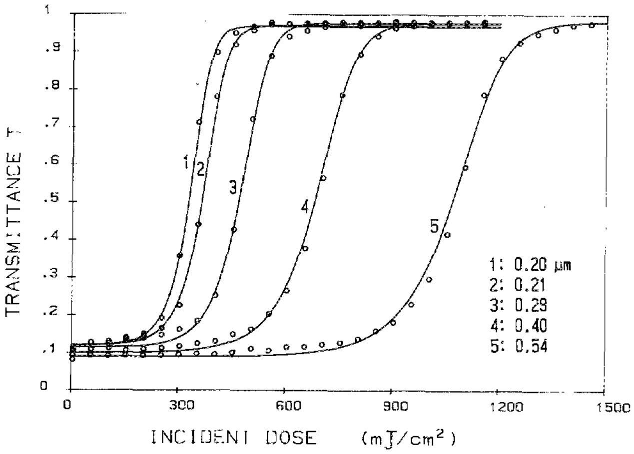

FIG. 2. Experimental (O, for purpose of clarity) and simulated (—) photobleaching curves of PDHS with various thickness.

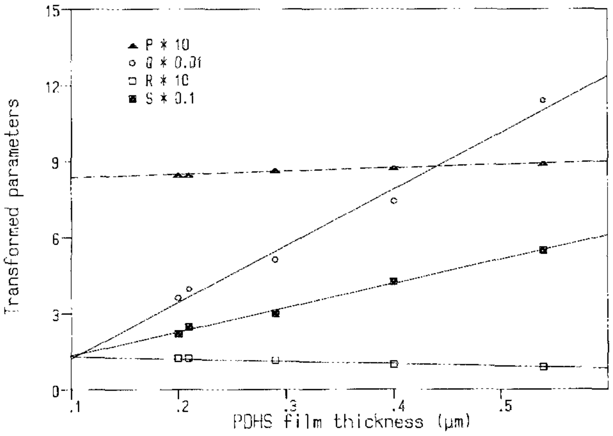

FIG. 3. Linear relationships of simulation parameters as a function of thickness of PDHS thin films.

film decreases from about 1.68 down to 1.45 with exposure doses up to about 240 mJ/cm^2 because of the cleavages of σ bonds of Si–Si backbones. The automatic modeling and profile simulation are impractical for CEL studies in such a case.

An equation was derived to fit these nonlinear photobleaching curves [Table I]. Both thin film transmittance at specific incident doses and transmitted doses can then be calculated. The fitting results are shown as solid lines in Fig. 2. Four parameters, namely P, Q, R, and S are used in this equation. P is defined as a transmittance change related parameter before and after bleaching, and is similar to the parameter A of Dill's model. Q is a film thickness related parameter, R the transmittance of the unbleached film, and S the slope related parameter at the inflection point of the bleaching curve. Linear relationships were found for these four parameters as a function of PDHS thin film thickness as shown in Fig. 3 within the usually used thickness range for CEL. This equation can apply to different thickness of PDHS film based on this linearity which Dill's model does not take into account.

TABLE I. Equations used for modeling and simulations.

$$T(D_i) = P\left[1 - \frac{1}{\exp[(D_i - Q)/S] + 1}\right]^{1/2} + R,$$

$$D_t = \int_0^{D_i} T(D_i)\,dD_i$$

$$= 2PS\ln(\sqrt{1+e^u} + \sqrt{e^u})\Big|_{u_0}^{u} + RD_i,$$

$T(D_i)$: film transmittance at D_i,
D_i: incident dose,
D_t: transmitted dose,
P: transmittance change parameter,
Q:film thickness related parameter,
R:transmittance of unbleached film,
S:slope related parameter at inflection point,

$$u = \frac{D_i - Q}{S},$$

$$u_0 = \frac{-Q}{S},$$

The enhanced contrasts calculated for different PDHS film thickness are shown in Fig. 4 using 0.3 for contrast of the aerial image. Transmitted doses calculated from the derived equation are also shown. From Fig. 4, we can find that the enhanced contrast does not improve further with thicker PDHS film. A three-dimensional (3D) plot of enhanced contrast versus different contrast level in the aerial image and dose is shown in Fig. 5. The range of maximum enhanced contrast becomes much broader for aerial image contrast higher than 0.6. This is certainly an advantage for the process control of exposure dose. The gain is the ratio

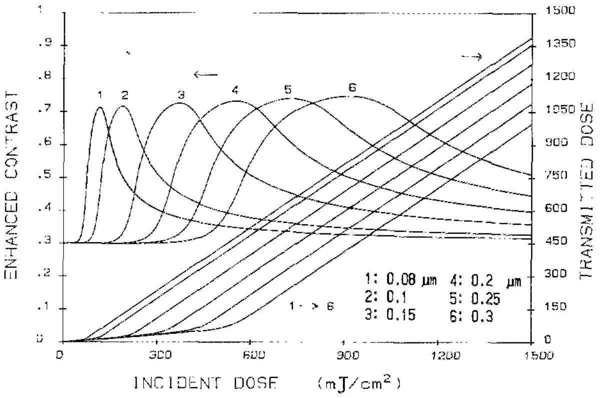

FIG. 4. Simulated curves of enhanced contrasts (using 0.3 for aerial image) and transmitted doses as a function of incident doses for different thickness of PDHS thin films.

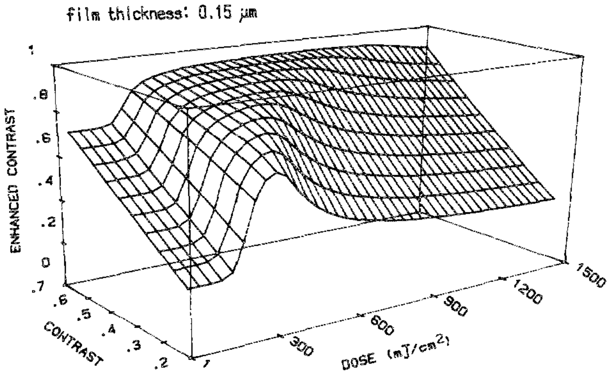

FIG. 5. 3D plots of enhanced contrast vs incident doses for various contrasts of aerial images.

TABLE II. Nominal parameters used for CEL modeling and profile simulation.

Projection system:	Resist parameters (AZ-1350J):
Wavelength = 365 nm	$A = 0.9\ \mu m^{-1}$
NA = 0.315	$B = 0.316\ \mu m^{-1}$
$\sigma = 0.7$	$C = 0.012\ cm^2/mJ$
Space = 0.5 μm	Refractive index = 1.65
Pitch = 1.0 μm	Thickness = 1.0 μm
Defocus = 0	
CEL parameters:	Developer conditions:
Thickness = 0.11 μm	Develop time = 11 s
C (aerial image contrast) = 0.60	$R_{max} = 500$ nm/s
C′ (enhanced contrast) = 0.91	$R_{min} = 0.5$ nm/s
Exposure doses = 870 mJ/cm^2	$n = 5.0$
Transmitted doses = 300 mJ/cm^2	$mTH = 0.61$
P: 0.838 R: 0.130	
Q: 140 S: 14.20	

$P = 0.127\times\text{thickness}(\mu m) + 0.824$
$Q = 2247\times\text{thickness}(\mu m) - 106.7$
$R = -0.0934\times\text{thickness}(\mu m) + 0.140$
$S = 95.6\times\text{thickness}(\mu m) + 3.682$

between enhanced contrast and aerial image contrast as illustrated in Fig. 6. The results indicate that the gain is nearly independent on its thickness for PDHS. The very high exposure doses (higher than 900 mJ/cm^2) cannot be used because of the phenomenon of self-development of PDHS film. For the studies of CEL, the parameters in Table II are used for the simulations of photoactive compound (AZ-1350J) concentration at the surface of the bottom layer, and sidewall profile (1 μm thickness of AZ-1350J) after wet development (Fig. 7). PROLITH was recompiled and modified to do the simulations along with the use of the abovementioned equation. The results of Fig. 7 show that the use of PDHS as a contrast enhancement layer does improve the sidewall angle somewhat. The drawback is the need for higher exposure dose.

Figure 8 shows that the reported nonlinear bleaching curve of CEM-2 can be modeled quite well by the use of this equation. The values of fitted parameters are also shown. The same equation can also simulate the nonlinear bleaching curves of *p*-diazo-*N*,*N*-dimethylaniline chloride zinc chloride very well and will be presented in another paper soon.

IV. CONCLUSIONS

The parameters of the derived simulation equation are linear with PDHS film thickness within nominal thickness range of 0.1–0.6 μm for CEL. Based on this linearity, simulation of CEL behavior is more accurate than those using Dill's model. The enhancement of contrast seems to be inde-

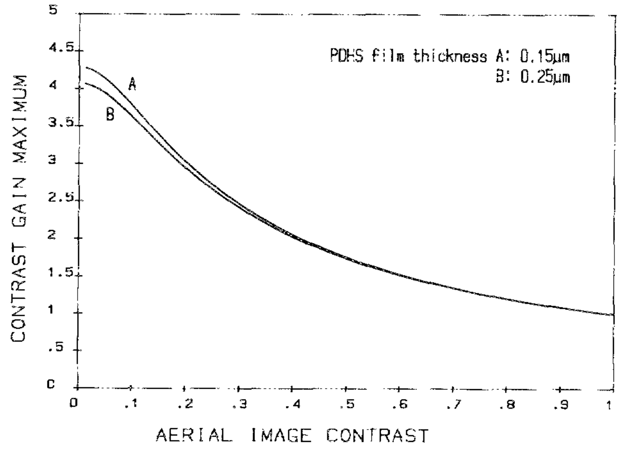

FIG. 6. Plots of gains vs contrasts of aerial images.

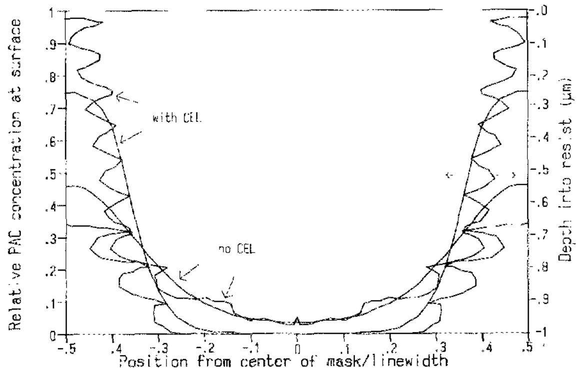

FIG. 7. Simulated concentrations of photoactive compound (PAC), (AZ-1350J), at surface after exposure, and sidewall profiles after wet development with and without CEL.

pendent of thickness of PDHS within these ranges. The same equation also fits the reported nonlinear photobleaching curve of CEM-2 quite well.

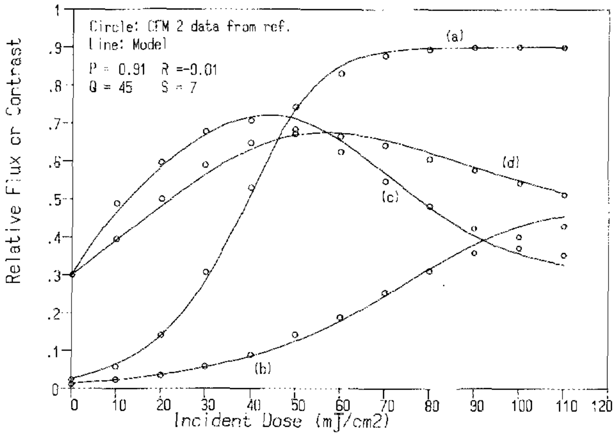

FIG. 8. Reported (O, data from Ref. 4) and model simulated (solid line) curves of CEM-2: transmitted flux at maximum (a), at minimum (b); instantaneous (c) and integrated (d) contrast.

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