An Investigation of Spin Coating of Electron Resists

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This paper reports the results of spin coating studies of an electron resist using several different solvents. Two problems which were frequently observed during the spin coating studies were the appearance of orange peel coatings and the formation of cloudy films. The appearance of orange peel is attributed to the rapid drying of low-boiling solvents. The formation of a cloudy film is believed to be caused by the hygroscopic nature of the solvents used. The resist film thickness can be approximated by the relationship $l = KC^{2.1}/\omega^{0.5}$, where l is film thickness, C is volume fraction of polymer resist, K is a constant and ω is the rotation speed. The results are compared with the theoretical modelings of Washo (1) and Meyerhofer (2).

INTRODUCTION

The spin coating process has been widely used for depositing electron resist film on the surface of a substrate. The process is relatively simple and convenient, and it usually produces uniform films which are quite reproducible. However, it is generally known that the uniformity of the film greatly depends on the solvent used. For a given polymer and under given operating conditions, certain solvents may produce uniform films while some others may not. If there are many solvents available for a particular polymer resist, what are the criteria for selecting a right "spinning" solvent? If the choice of solvent is limited due to the poor solubility of the polymer, and the available solvent does not produce a uniform film, what are the main parameters one must consider to improve the uniformity?

This paper reports the results of spin coating studies of a negative electron resist using several different solvents. To provide some clues to the above questions, an attempt has been made to correlate the film characteristics with the material and process parameters of the spin coating process.

EXPERIMENTAL

Resist Synthesis and Characterization

The negative electron resists used in the present study were the copolymers of styrene and glycidyl methacrylate. The synthesis and characterization of resists have been reported previously (3). The characterization of the resists are shown in *Table 1*. Polymer A and polymer N differ slightly in composition and molecular weight. The intrinsic viscosity of the polymer A was determined in chlorobenzene (CB), methyl ethyl ketone (MEK) and dimethylformamide (DMF) at 27°C using the conventional method. The molecular weight distribution of the polymers (MWD, $\overline{M}_w/\overline{M}_n$) was determined by a Water Associate Model 202 gel permeation chromatograph. The glass transition temperatures of the polymers were determined by a DuPont 990 differential scanning calorimeter. The solubility parameters of the polymer resists were calculated according to the group contribution method of Hoy (4).

Solvents

Reagent grade chlorobenzene (CB), dimethylformamide (DMF), methyl ethyl ketone (MEK) and methylene chloride (MC) were used as received. The relevant physical constants of the solvents were mostly taken from Ref. 5 and are shown in *Table 2*. The solubility parameter of the solvents were taken from Ref. 6.

Polymer Solutions

The viscosity of the polymer solutions used in spin coating was measured as a function of shear rate at 27°C using a Cannon-Ubbelohde four-bulb shear dilution viscometer. The results are shown in *Table 3*.

Table 1. Characterization of Polymers

Polymer	Composition, mole percent styrene	Intrinsic viscosity at 27°C*			MWD	T_g °C	Solubility** Parameter
		CB	MEK	DMF			
Polymer A	28.4	0.82	0.63	0.97	2.2	72	9.8
Polymer N	28.7		0.56		2.2	73	9.8

* CB, chlorobenzene; MEK, methyl ethyl ketone; DMF, dimethylformamide.
** Calculated values.

Table 2. Characterization of Solvents

Solvent	T_b, °C	Solubility param- eter	Water solubility at 20 deg g/100 g H_2O
Chlorobenzene	131.7	9.5	0.0488
Methyl ethyl ketone	79.6	9.3	35.31
Dimethylformamide	152.8	10.6	Completely miscible
Methylene chloride	40	9.7	2

Table 3. Viscosity of Polymer Solutions as a Function of Shear Rate

Polymer solution	Concentration, volume percent polymer	Viscosity, centistokes	Shear rate at wall, s^{-1}
Polymer N-CB	5.5	15.75	73.90
		15.67	44.14
		15.70	26.28
		15.74	14.88
Polymer N-CB	7.7	38.75	30.04
		38.90	17.77
		39.40	10.47
		39.10	5.91
Polymer N-CB	10.4	95.51	12.19
		96.32	7.17
		95.97	4.30
		96.32	2.40
Polymer A-MEK	6.3	15.34	75.87
		15.49	44.62
		15.42	26.75
		15.23	15.17
Polymer A-DMF	6.3	31.64	36.78
		31.46	21.97
		31.80	12.97
		31.66	7.30

Spin Coating

The resists were spin coated at various rotating speeds on 1 in. square glass substrates which were coated with a chromium film 0.07 μm thick. The spinner used was a Headway Model EC101 photo-resist/spinner. The electron resists were spin coated under air (65-75 percent humidity), dry N_2 atmosphere, and solvent vapor saturated atmosphere. The resist film was baked in a vacuum oven at 90°C for 30 min prior to thickness measurements. All reported resist films were dried films.

The film thickness was measured with a Bendix proficorder. The accuracy of the proficorder is about 3 percent.

RESULTS AND DISCUSSIONS

Effect of Solvents

The results of present studies are summarized in *Tables 4A* and *4B*. The four solvents used in present studies were MC, MEK, CB and DMF. The solubility parameters of the four solvents are 9.7, 9.3, 9.5 and 10.6, respectively. The calculated solubility parameter for the polymers is 9.8. The solvents appeared to be all "good" solvents and the polymer solutions obtained were all homogeneous. However, the boiling point of the solvents are quite different and so is the water solubility of the solvents. Two problems which were frequently observed during the present spin coating studies were (a) the appearance of "orange peel", and (b) the formation of "cloudy" films.

"Orange Peel" Films. The most common problem in the spin coating process has been the appearance of "orange peel" on certain films. The scanning electron micrograph of polymer A films obtained by using MEK as the spinning solvent is shown in *Fig. 1*. Comparison of *Table 4A* and *4B* indicates that orange peel appeared only when the low boiling solvents MC and MEK were used. Such observation suggests that rapid drying of the film during the spin coating process is the main cause for the orange peel formation. In a typical run, the spinner was turned on immediately after the substrate surface was covered entirely with the polymer solution and allowed to spin for one minute.

If rapid evaporation of low boiling spinning solvents is the main cause for orange peel formation, then its formation probably can be prevented by (a) spin coating under solvent vapor saturated atmosphere, and (b) reducing the spinning time.

To provide MEK vapor saturated atmosphere, the spinner was enclosed in a plastic box. A large piece of paper towel soaked with MEK was placed inside the box to provide a saturated vapor atmosphere. However, it was soon found that the orange peel formation could not be prevented by spin coating under this condition. This

Table 4A. Resist Film Characteristics Using High-Boiling Solvents

Spinning solution	Concentration, vol. percent polymer	Spinning, speed 1000 rpm	Atmosphere	Film characteristics	Film thickness, μm
Polymer N-CB	10.4	1	air	good	2.2
		2	air	good	1.6
		4	air	good	1.1
Polymer N-CB	7.7	1	air	good	1.3
		2	air	good	0.90
		4	air	good	0.62
Polymer N-CB	5.5	1	air	good	0.58
		2	air	good	0.44
		4	air	good	0.29
Polymer N-DMF	6.3	1.5	air	cloudy, O.P.*	
		1	N_2	good	0.68
		1.5	N_2	good	0.48
		3	N_2	good	0.31

* O.P. means the coating has "orange peel".

Table 4B. Resist Film Characteristics Using Low-Boiling Solvents

Spinning solution	Concentration, vol. percent polymer	Spinning speed, 1000 rpm	Spinning time, s	Atmosphere	Film characteristics	Film thickness, μm
Polymer A-MEK	6.3	1.5	60	air	O.P.*	
		6	60	air	O.P.	
		1.5	60	N_2	O.P.	
		6	60	N_2	O.P.	
		1.5	60	MEK	O.P.	
		6	60	MEK	O.P.	
		1.5	15	MEK	Good	1.59
		4	15	MEK	Good	0.90
		6	15	MEK	O.P.	
Polymer A-MEK	3.3	1.5	60	air	O.P.	
		1.5	60	MEK	O.P.	
		3	60	MEK	O.P.	
		6	60	MEK	O.P.	
Polymer A-MC	6.3	1.5	60	air	O.P.	
		1.5	60	N_2	O.P.	
		1.5	60	MEK	O.P.	

* O.P. means the coating has "orange peel".

was due to the fact that the spinner was not totally enclosed. The construction of the spinner was such that spacing was provided for the rotation of the spinner shaft. The spacing also provided a path for the circulation of the air in and out of the box during the spinning which induced the rapid evaporation of MEK. However, it has been found that if the spinning speed is not very high (<6000 rpm), the orange peel formation can be prevented by reducing the spinning time to 15 s., which is the approximate time required to slough off the bulk of the polymer solution (see *Table 4B*). Since higher spinning speed will induce faster circulation of air which increases the evaporation rate of the solvent, this observation is consistent with the suggestion that rapid drying of film is the main cause of the orange peel formation. Our subsequent controlled dip coating of polymer A using the two low boiling solvents MC and MEK further confirmed that when the evaporation rate was retarded by drying the film under solvent vapor atmosphere, orange peel formation could be successfully prevented.

"Cloudy" Films. The appearance of "cloudy" film was observed when the hygroscopic solvent DMF was used

Fig. 1. SEM micrograph (5000X) of Polymer A film which has orange peel.

in the coating. A SEM micrograph of a cloudy film is shown in *Fig. 2*. Since the formation of the cloudy film can be prevented by carrying out the spin coating under nitrogen atmosphere (*Table 4A*), its formation apparently was caused by the precipitation of the polymer due to the presence of excess amounts of water, absorbed by DMF during the spin coating process. It also appears that water affinity (or water solubility) of the solvent is the most important factor in determining the formation of cloudy or opaque films. Compared with DMF, the boiling point and water solubility of MC are both very low. Lower boiling point means higher solvent evaporation rate and, therefore, the "chilling" effect is more severe. However, MC has much lower water solubility. The water condensed on the surface of the wet film induced by the "chilling effect" apparently was limited to the surface and was transient, since no noticeable cloudy or opaque film formation was observed by using MC as the spinning solvent.

Film Thickness as a Function of Spinning Speed and Solution Concentration

The film thickness is mainly determined by the concentration (or the viscosity) of the polymer solutions and the rotating speed of the spinner. The resist film thickness l vs rotating speed ω is plotted in *Fig. 3* for several polymer solutions. The $\log l$ vs $\log \omega$ plots appear to be all linear which suggest the following relationship $l = k\omega^\alpha$, where both k and α are constant. The slopes of the six lines, a, a', b, b', c and c' are (−0.52), (−0.50), (−0.63), (−0.55), (−0.57) and (−0.50), respectively. This suggests that $l = k\omega^{-0.54}$.

The effect of concentration on the resist film thickness at a given rotating speed is shown in *Fig. 4*. The $\log l$ vs $\log C$ plots, where C is volume percent of polymer, again appear to be all linear which suggests the relationship $l = k'C^{\alpha'}$, where both k' and α' are constant. The slopes of the six lines a, a', b, b', c and c' are 2.08, 2.18, 2.06, 2.17, 2.09 and 2.28, respectively. The $\log l$ vs $\log \mu$ plots, where μ is the solution viscosity, did not appear to be linear and therefore are not shown. The results suggest
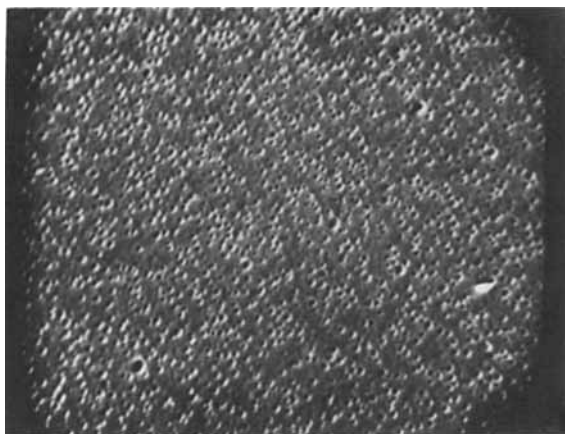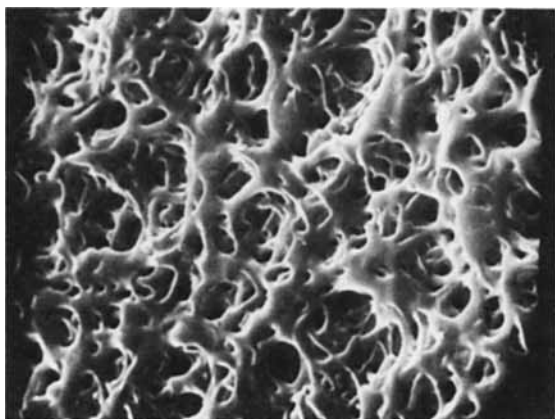
Fig. 2. *SEM micrograph (5000X) of a "cloudy" film (polymer A, using DMF as the spinning solvent).*
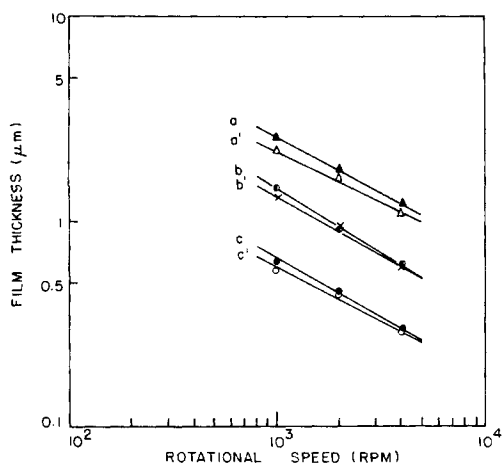

Fig. 3. *Film thickness vs rotating speed. The concentration of polymer solutions a, b, c are 10.4, 7.7 and 5.5 volume percent respectively, 15 s spinning time. The prime indicates longer spinning time, 60 s.*
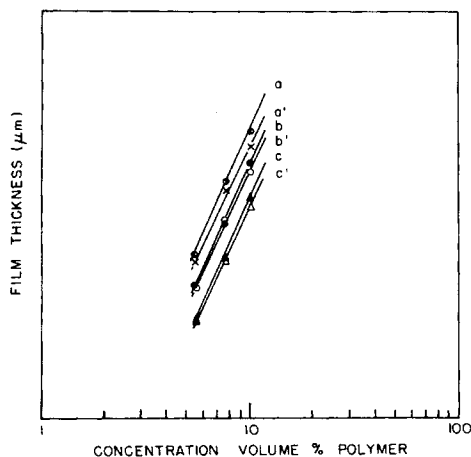

Fig. 4. *Film thickness vs solution concentration. The rotating speed for a, b, c, are 1K, 2K and 4K rpm respectively, 15 s spinning time. The prime indicates longer spinning time, 60 s.*

that $l = k'C^{2.1}$ or $l = KC^{2.1}/\omega^{0.54}$ which is in agreement with Damon's experimental results on Kodak photoresists (7).

The rheology of the spin coating process has been studied by Washo (1). Based on the assumptions that (a) the spinning fluid is Newtonian, (b) constant volumetric fluid flow on and off the disk, (c) no evaporation loss of solvent (therefore μ is constant), and (d) no body or surface force, Washo has predicted that the slope of $\log l$ vs $\log \omega$ plot to be (-0.67) and the slope of $\log l$ vs $\log C$ to be 2.47, i.e., $l = kC^{2.47}/\omega^{0.67}$.

The results obtained from viscosity vs shear rate studies (*Table 3*) indicate that the spinning solutions used in the present studies are all Newtonian. The absolute values of α obtained from present studies are all approximately 0.5, which is smaller than Washo's theoretical value (-0.67). The value $\alpha' = 2.1$ obtained from our studies is also smaller than Washo's theoretical value of 2.47.

It is believed that the difference between our experimental values and Washo's theoretical values is due to the fact that in the actual coating process Washo's assumption (c) was not strictly held, i.e., evaporation loss of solvent (chlorobenzene) did occur. Meyerhofer (2) has presented a model for the spin coating process which takes into account the evaporation of the solvent. Using only the centrifugal force, linear shear forces and uniform evaporation of the solvent, the thickness of the film and the time of drying were calculated as functions of the various processing parameters. The model was found to be in agreement with the experimental results obtained on positive photoresists. Meyerhofer has found that the film thickness l shows the following dependence on spin speed ω, initial viscosity V_0 and evaporation rate e, $l \propto \omega^{-2/3} V_0^{1/3} e^{1/3}$. Further he has found that e is proportional to $\omega^{1/2}$.

Meyerhofer's prediction is in agreement with Washo's theoretical model, i.e., $l \propto \omega^{-2/3}$ if there is no evaporation loss of solvent. If e is proportional to $\omega^{1/2}$ as suggested by Meyerhofer, then his model predicts that $l \propto \omega^{-1/2}$ which is in agreement with our experimental results as well as Damon's (7).

It is reasonable to assume that some evaporation of the solvent, chlorobenzene, occurred during the spin coating. Although chlorobenzene is not a highly volatile solvent, some evaporation loss of chlorobenzene cannot be totally avoided due to the continuous flow of fresh air onto the surface of the spinner during the spin coating (8). This is particularly true at higher spin speeds. Since evaporation loss of solvent tends to make the spinning solution more viscous which results in a thicker film, this explanation is consistent with the observations found in this study, i.e., the smaller slope in the $\log C$ vs $\log \omega$ plot.

ACKNOWLEDGMENT

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