193nm CD shrinkage under SEM: modeling the mechanism

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ABSTRACT

As photolithography platforms move from 248nm to 193nm resist systems, the industry's established dimension measurement technique (CD-SEM) causes significant shrinkage of the resist structures during measurement. Many studies have been done to characterize this effect and look for the factors that influence / reduce this shrinkage. While numerous anecdotal mechanisms have been proposed to explain the shrinkage, few theoretical / empirical equations have been proposed to connect the observed effects to fundamental mechanisms.

Models are proposed relating physical properties (accelerating voltage, photoresist density, resist e-beam film shrinkage) to the commonly observed CD 'hammer test' shrinkage profiles. The validity of the model assumptions is tested via Monte Carlo simulations, FTIR, e-beam curing, SPM and ellipsometry. These models explain the shape of the CD response to repeated measurements (exponential decay curve) and the magnitude of the shrinkage. These models also offer insight into why lower accelerating voltages cause reduced CD shrinkage, although the models predict that accelerating voltage should be a much more dominant parameter for CD shrinkage than literature has shown to date. Mass loss and density changes were also characterized during e-beam cure to check the validity of the model assumptions.

Keywords: SEM, electron, 193nm photoresist, shrinkage, linewidth slimming

1. BACKGROUND

Currently all 193nm photoresist platforms (acrylate, COMA, VEMA, hybrids) suffer from significant (>3nm) linewidth slimming under the SEM due to electron-photoresist interactions, some worse than others. For example, several studies have noted that acrylates show more SEM shrinkage than COMA resists.[4,7,8] Past studies have determined excellent clues towards understanding what influences the shrinkage. Higher SEM accelerating voltages cause greater amounts of CD shrinkage during 'hammer tests' or repeated measurements on the same feature.[1,2,4,5,8] Beam current appears to have a minimal effect on this line slimming, at least for the first hundred measurements or so.[1,2,8] The magnitude of the CD shrinkage appears absolute, independent of feature size, implying a surface phenomenon.[2,8]

Interesting results have been noted w.r.t. e-beam cure systems, both in the area of characterization of the slimming effect and in the area of controlling the shrinkage. All 193nm photoresists currently contain carbonyl groups; curing of these thick (1000A+) resist films with highly accelerated electrons (several keV) causes 15-30% film thickness shrinkage and the disappearance/conversion of the carbonyl groups.[3,5,6,7] E-beam curing of 193nm photoresist structures has also been shown to minimize/eliminate subsequent SEM measurement shrinkage;[2,3,6] perhaps this cure process could be used as a preparation step prior to SEM metrology.

Hammer testing CD results for 193nm resists show the CD shrinkage follows an exponential decay response, with the most shrinkage seen during the first few measurements and an eventual stabilization in CDs after many (100+) measurements. Unfortunately, the first few measurements are key for lithography; the shrinkage during the first measurement provides barriers to calibration accuracy, and the shrinkage during second and third measurements makes it impossible to remeasure problem sites in the exact same location. Studies have noted that a three-term exponential decay equation offers the best fitting of the CD shrinkage response, and possible mechanisms (solvent loss, chain scission, etc.) have been assigned to each of the three terms.[1,4]

This study was intended to offer some new ways of modeling the linewidth shrinkage. Models are most useful when their assumptions are clearly defined, and predictions about real-world behavior can be made from them. We will first define and discuss two linewidth shrinkage models. The results from several experiments will then be used to test the real-world predictions and evaluate a few of the model assumptions.

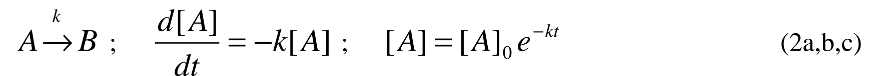
2. LINEWIDTH SHRINKAGE MODELLING

2.1 Limitations of empirical fitting to the three-term exponential decay equation

As previously mentioned, some of the linewidth shrinkage mechanism modeling has involved the use of a three-term exponential decay equation such as Equation 1:

$$CD = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} + a_3 e^{-t/\tau_3} \tag{1}$$

Eq.1 implies that the CD is affected by three parallel first-order rate equations, each equation constructed from kinetics such as those in Equations 2a,b,c:



$$A \xrightarrow{k} B \ ; \quad \frac{d[A]}{dt} = -k[A] \ ; \quad [A] = [A]_0 e^{-kt} \qquad \text{(2a,b,c)}$$

In Eq.2, [A] represents the concentration of a given species A (such as solvent), and k represents a rate constant governing the speed of the reaction. Studies with some success been done attempting to identify the exact species loss associated with all three first-order reactions through modulation of chemical groups and processing conditions.[1,4] However, it can be difficult to theoretically relate the time constants τ_i and amplitude constants a_i to the species loss mechanisms.

As an alternative to the three-term exponential decay empirical fitting, models were constructed by making several assumptions about electron behavior in the photoresist. One advantage to this technique is that time constants and amplitude constants of the CD slimming can be theoretically connected to the phenomena that cause them. The first step in an e-beam photoresist shrinkage model is to define how far the electrons penetrate the photoresist.

2.2 Electron penetration depth of the photoresist

The distance that electrons penetrate into the photoresist is traditionally determined via integration of the theoretical Bethe equation or by Monte Carlo simulation. Simplified empirical expressions are available to relate the electron penetration depth to substrate density and accelerating voltage. The Grün Range (R_g) is perhaps the simplest of these:[9]

$$R_g\,(\mu m) = \frac{0.046}{\rho} V_{acc}^{1.75} \tag{3}$$

where ρ is substrate (photoresist) density and V_{acc} is the accelerating voltage of the incident beam. The assumption will be made in the following three models that the Grün Range represents the maximum electron penetration depth. Electron penetration depth data from studies on a variety of materials including carbon and silicon dioxide show this penetration depth – accelerating voltage relationship is valid for SEM electrons (0.3 – 1.0keV).[10]

When the electron beam in a SEM strikes the top of a photoresist structure, the "vertical" penetration depth is assumed to be the Grün Range. However, both of the models proposed in this paper assume this "topside" penetration is not as critical to linewidth shrinkage as "sidewall" or lateral penetration. Even if the resist sidewall is perfectly vertical (perpendicular to substrate), a portion of the electron beam can backscatter off the substrate near a resist sidewall and bounce into this sidewall. Monte Carlo (MC) simulations were used to estimate the lateral penetration depth at 20-30% of the vertical penetration depth.

2.3 Defining the Simple Shrinkage model
The Simple Shrinkage model is constructed with the following set of assumptions:
[A1] The Grün Range accurately reflects the electron penetration depth
[A2] The lateral (sidewall) penetration depth **d** is 25% of the vertical (topside) penetration depth $\mathbf{R_g}$
[A3] Resist density does not change during exposure to the electron beam
[A4] Unexposed photoresist shrinks by a constant percentage α upon the interaction with the electron beam

- The electron dose is sufficiently high throughout the full penetration depth to cause the shrinkage reaction
- All shrinkage occurs during the first exposure; subsequent interactions of exposed resist to the electron beam have no effect

[A5] All CD shrinkage occurs before the actual measurement is taken

Assumptions #1 and #2 were previously discussed in Section 2.2; Assumption #3 (density unchanged by electron beam interaction) will be measured in Section 3.4 to follow. Assumption #4 states there are only two classes of photoresist, unexposed and exposed. If the film shrinkage coefficient α is 0.1, little film shrinkage occurs, whereas if α is 0.9, most of the film shrinks during exposure. This film shrinkage coefficient α intuitively relates well to the film thickness measurements taken during e-beam cure experiments. Assumption #4 is clearly an oversimplification of reality, and will become slightly more refined in the next model.

Assumption #5 addresses a timing issue. In a real measurement, the electron beam will sweep over the target area many times to gain sufficient signal-to-noise. A good chance exists that resist shrinkage occurs between the first sweep and the last sweep, leading to a CD measurement somewhere in-between the initial true CD (pre-measurement) and the final true CD (post-measurement). Assumption #5 simplifies this by assuming the electron beam first has a full interaction with the sample, followed by a measurement of the final true CD.

Based on these five assumptions, the Simple Shrinkage theoretical model can be constructed. The derivation is provided in the Appendix (equations A1-A15). The following three analytical relations emerge from the derivation:

$$\Delta CD = A\left[1 - e^{-meas/\tau}\right] \tag{4}$$

$$\alpha = e^{-1/\tau} \tag{5}$$

$$0.25R_g = d = A\frac{1-\alpha}{2\alpha} \tag{6}$$

Eq.4 shows that this extremely simplified model predicts an exponential decay response, which is in agreement with reality. Eq.5 & 6 show the simple relationship between the two constants $\{A, \tau\}$ of the CD shrinkage equation (Eq.4) to the more fundamental properties α (film shrinkage coefficient) and R_g (vertical electron penetration depth). The validity of the relationships in Eq.5 & 6 will be assessed via empirical results in Section 3.2.

2.4 Multi-Dose model
In the Simple Shrinkage model, all of the resist shrinkage occurs upon the first electron interaction (Assumption 4). However, if this assumption were true we might expect thick films of photoresist to dramatically shrink with only the lightest of doses in electron cure systems, which isn't the case. It seems a better assumption would allow for the film shrinkage to occur over several electron interactions (measurements).

The new assumption in this model that replaces Assumption 4 from the Simple model is defined in the following way:

- The first electron-resist interaction with unexposed resist will cause a constant α_1 amount of film shrinkage throughout the full electron penetration depth
- We define a shrinkage decay constant β (less than 1); subsequent exposures of this exposed resist will have reduced film shrinkage determined by α_1 and β. For example, the second film exposure will shrink by $\alpha_1\ \beta$, the third exposure $\alpha_1\ \beta^2$, etc.

Unfortunately, this more complicated assumption results in a more complex set of equations and must be solved numerically (see Appendix, A16-A25). However, several empirical relationships were established:

$$\alpha_{total} = \frac{1}{2\left[\mathrm{d}/\mathrm{A}\right]+1} \tag{7}$$

$$\alpha_1 \sim \frac{1-e^{-1/\tau}}{2\left[\mathrm{d}/\mathrm{A}\right]} \tag{8}$$

$$\beta \sim 1-\frac{1-e^{-1/\tau}}{1-e^{-1.2\sqrt{d/A}}} \tag{9}$$

In Equation 7, α_{total} represents the total film shrinkage after an infinite number of exposures; note that Equation 7 is merely a rearrangement of Equation 6 from the Simple model. The Multi-Dose model shows a second similarity to the Simple model, in that the CD shrinkage exhibits an exponential decay response (Equation 4). Results from the Multi-Dose model will be compared to empirical results in Section 3.3.

More advanced models than these two (Simple and Multi-Dose) are certainly possible to construct by further modification of Assumption 4. For example, the electron dose distribution is clearly not uniform throughout the full penetration depth (an assumption made for both of the defined models in this paper). However, it should be noted that these advanced models will always predict smaller CD shrinkage amplitudes than the Simple and Multi-Dose models.

3. EXPERIMENTAL TESTING OF MODEL VALIDITY

3.1 Experimental estimates for film shrinkage coefficients

Two resists were tested in this study, Sumitomo PAR710 and JSR AR237J. Film shrinkage values of ~25% have previously been published for PAR705 at high (4000μC/cm^2) electron cure doses.[3] Silicon wafers were coated with 3500A of JSR AR237J, e-beam cured on an ElectronCure™ 1200-PR over a range of doses at 3.75keV and 6mA. Film thicknesses were measured both on a M-88 Spectroscopic Ellipsometer and a Veeco D9000 AFM. The two thickness measurement techniques offered similar results, and AR237J showed similar high-dose film shrinkage (~25%) to the PAR705.

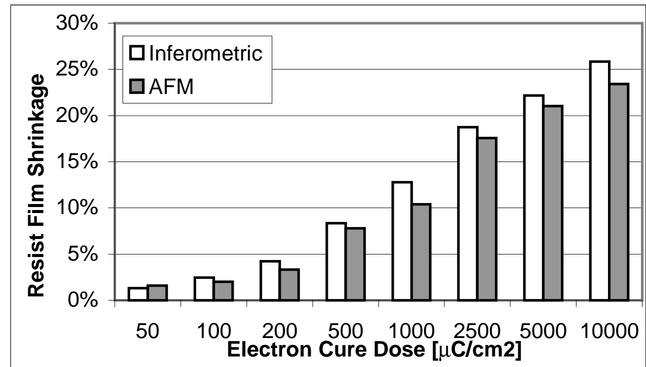


Figure 1: AR237J resist film shrinkage vs. electron cure dose

3.2 Simple Shrinkage model predictions vs. empirical results

Numerous runs of repeated CD measurements ('hammer tests') were taken using an AMAT VeraSEM3D with beam settings of 10pA and accelerating voltages of 0.3, 0.5 and 0.8 keV. 120nm 1:1 line:space structures were measured for two resists, Sumitomo PAR-710 and JSR AR237J. Three example measurement runs for each accelerating voltage are shown below in Figures 2 & 3. Note that higher accelerating voltages correspond to greater shrinkage effects; this observation has been observed numerous times in past literature.

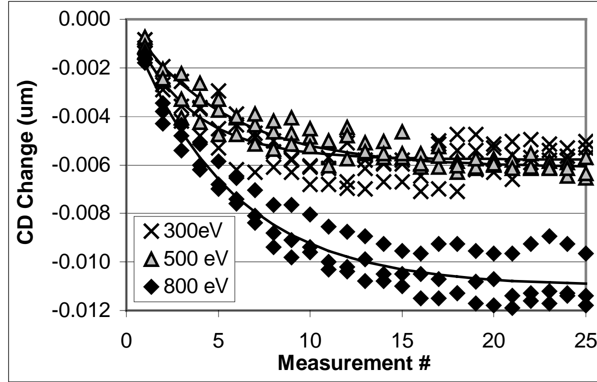


Figure 2: PAR710 CD shrinkage vs. accelerating voltage

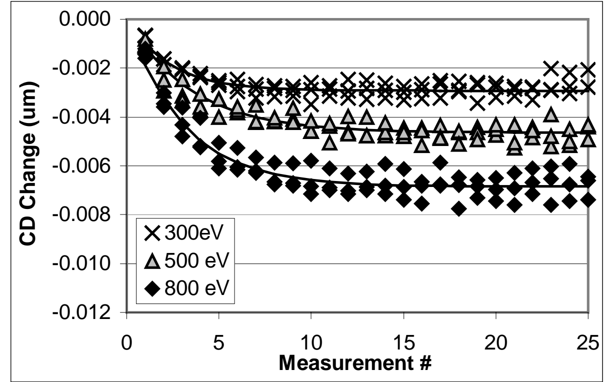


Figure 3: AR237J CD shrinkage vs. accelerating voltage

Calculation of these CD changes requires an initial CD value – a linear approximation was made on the first three measurements to extrapolate the initial CD. The CD changes were also corrected for carbonization effects (i.e. linear growth per measurement) to isolate the CD shrinkage signatures. A single exponential decay curve (see Eq.5) was fit to each run, generating estimates for τ and A.

The τ estimates ranged from 2-7 measurements for both resists. According to the Simple Shrinkage model (equation 5), these values of τ should correspond to film shrinkage coefficient α values of 0.65 – 0.85, meaning that 65-85% of the film thickness is shrunk during film exposure. These shrinkage coefficient predictions are way too high, compared with the experimental film thickness shrinkage measurements of 25%. The real-world shrinkage mechanism appears much slower than the Simple Shrinkage model, quite probably due to the oversimplified assumption that the entirety of the resist shrinkage occurs after only one exposure.

The amplitude estimates A for PAR710 ranged from 5-12nm (depending on accelerating voltage), vs. amplitudes for AR237J ranging from 3-7nm. The Simple Shrinkage model (equation 6) can be used to predict A using three parameters: the Grün Range, the ratio of lateral to vertical penetration $\mathbf{r_{lv}}$, and the shrinkage coefficient α (with experimental estimates of 0.25 for both resists). While real-world data are available to confirm the validity of R_g and α, r_{lv} can only be estimated through Monte Carlo simulations. Table 1 compares the experimental and modeled amplitudes using three values of r_{lv}. A lateral-vertical ratio of 0.25 corresponds to the Monte Carlo simulation estimate, while ratios of 0.65 and 1.00 cause the modeled amplitudes to agree more with experimental amplitudes.

Resist	Acc. Voltage [keV]	Experimental Amplitude [nm]	Model Amp. [r_{lv} = 0.25]	Model Amp. [r_{lv} = 0.65]	Model Amp. [r_{lv} = 1.00]
PAR710	0.3	6	0.8	-	3
PAR710	0.5	6	1.9	-	8
PAR710	0.8	11	4.3	-	17
AR237J	0.3	3	0.8	2	-
AR237J	0.5	5	1.9	5	-
AR237J	0.8	7	4.3	11	-

Table 1: Experimental vs. Simple model CD shrinkage amplitudes

When the Monte Carlo estimate for r_{lv} is used to predict CD shrinkage amplitudes, these modeled amplitudes are significantly smaller than observed shrinkage effects. Values for the lateral-to-vertical ratio of ~0.65 provides a better modeling match for the AR237J, and r_{lv} of ~1.00 models the PAR710 better. Experiments and / or more simulations are still needed to obtain better estimates of this penetration ratio.

The Simple model predicts that the CD shrinkage will have an exponential decay response, which is experimentally observed. This model predicts the CD shrinkage will happen much faster than experimentally observed, likely tied to the assumption that the shrinkage effect is complete during the first electron interaction. This model predicts much smaller CD shrinkage amplitudes than experimentally observed using the MC estimate for the lateral to vertical penetration ratio, although amplitudes for model vs. experimental can be brought into closer agreement by increasing this penetration ratio.

3.3 Multi-Dose model predictions vs. empirical results

One consequence of the fact that Equations 6 (Simple model) and 7 (Multi-Dose model) are equivalent formulas is that all CD shrinkage amplitude estimates given in the previous Section 3.2 are also true of this model. The primary difference between the two models relate to predictions of time constants. The Simple model predicted a much faster shrinkage reaction than experimentally observed. Stated another way, the τ predictions of the Simple model were significantly smaller than experimental values.

The primary advantage of the Multi-Dose model is that the time constant τ is no longer directly linked to the total shrinkage coefficient α_{total} (as in Equation 5 of the Simple model), but now can be fit using the two parameters α_1 and β. While the Simple model assumed that complete film shrinkage occurs on the first electron interaction, the Multi-Dose model allows for the shrinkage to occur over several electron-resist interactions. Table 2 contains estimates for the number of measurements needed to achieve complete (>98%) film shrinkage. Since there is uncertainty in the ratio of lateral to vertical penetration depths, the number of measurements is calculated for three ratio values.

Resist	Acc. Voltage [keV]	Exp. Time Constant [#meas]	Model Time Constant [#meas]	Number of Meas. [r_{lv} = 0.25]	Number of Meas. [r_{lv} = 0.50]	Number of Meas. [r_{lv} = 0.75]
PAR710	0.3	3.3	3.3	3	6	8
PAR710	0.5	5.2	5.2	11	14	16
PAR710	0.8	5.5	5.5	13	16	17
AR237J	0.3	2.3	2.3	3	6	7
AR237J	0.5	3.5	3.5	8	11	12
AR237J	0.8	3.1	3.1	9	11	11

Table 2: Multi-Dose time constant fitting – number of measurements needed for complete film shrinkage

While the Multi-Dose model allows for the experimental time constants to be perfectly fit by adjusting α_1 and β, one of the model's disadvantages is that these two parameters (α_1 and β) are not directly measurable properties and difficult to experimentally validate. However, sanity checks are possible by comparison of SEM electron doses to e-beam cure doses. The Multi-Dose model estimates that, depending on the ratio of lateral to vertical penetration depth, both resists needed between three and seventeen resist-electron interactions to complete the film shrinkage reaction (refer to Table 2 above). The electron dose of one SEM measurement was estimated at 250 $\mu C/cm^2$. The electron cure dose needed to complete the film shrinkage reaction was roughly 5000 $\mu C/cm^2$ (refer to Figure 1). From these two values, we can guess that the resist film requires roughly 20 measurements in order to complete the shrinkage reaction. This estimate of 20 measurements is somewhat higher than the Multi-Dose model predictions (3 – 17) but within the same ballpark.

3.4 Challenging the density assumption

Both models currently assume the photoresist density remains unaffected by interactions with the electron beam. While previous studies have noted film thickness loss during electron curing, mass loss and/or density changes during electron interaction have not been quantified. AR237J weight measurements were taken before cures, after cures, and after resist removal on a Sartorius microbalance. Experimental parameters are detailed in Section 3.1. Figure 4 compares the change in thickness to the change in mass as a function of electron cure dose. Figure 5 shows how density is affected by electron cure dose.

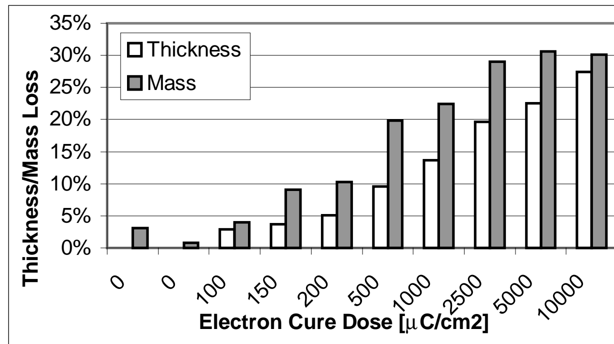


Figure 4: AR237J thickness and mass loss vs. cure dose

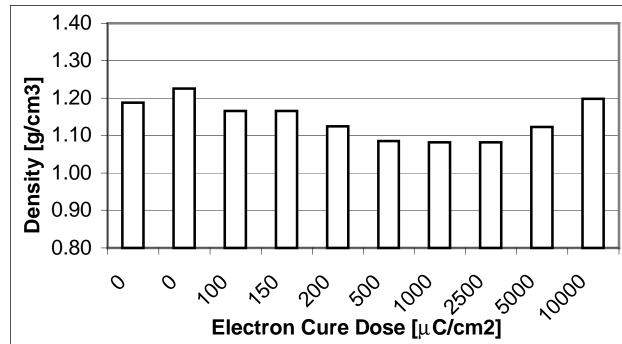


Figure 5: AR237J density vs. electron cure dose

The assumption of constant density (Simple Model assumption #3) appears accurate to within 10% throughout the electron curing process. If the proposed models in this paper are not valid, the fault of the model(s) will likely not be due to the constant density assumption.

3.5 Examination of the relationship between accelerating voltage and CD shrinkage

Quite a few papers have published results showing reduced CD shrinkage by lowering the accelerating voltage. Both of the models presented in the paper show CD shrinkage proportional to electron penetration depth, which is proportional to accelerating voltage raised to the 1.75 power. Is this relationship between CD shrinkage and accelerating voltage in fact observed? Shrinkage results from this study, along with five sets of previously published data, were compared in Table 3 below.

Reference	Parameters	AccV #1 [eV]	Shrinkage #1 [nm]	AccV #2 [eV]	Shrinkage #2 [nm]	Exp. CD Shrinkage Ratio [#1 / #2]	Model CD Shrinkage Ratio [#1 / #2]	Exp. AccV Coeff.	Model AccV Coeff
(Ours)	PAR710, 10pA, 25meas	800	11	300	6	1.8	5.6	0.62	1.75
(Ours)	AR237J, 10pA, 25meas	800	7	300	3	2.3	5.6	0.86	1.75
1	10pA, 100meas	600	25	400	18	1.4	2.0	0.81	1.75
2	PAR722, 4pA, 10meas	800	9	300	5	1.8	5.6	0.60	1.75
4	Acrylate, 10pA, 10sec	600	13%	400	6%	2.2	2.0	1.91	1.75
5	Acrylate, 2pA, 300sec	500	14	300	12	1.2	2.4	0.30	1.75
8	PAR700, 8pA, 10meas	800	15.5	300	6.5	2.4	5.6	0.89	1.75
8	AT111S, 8pA, 10meas	800	10	300	6	1.7	5.6	0.52	1.75

Table 3: Comparison of CD shrinkage results vs. accelerating voltage

While both models predict that CD shrinkage should be proportional to accelerating voltage raised to the 1.75 power, experimental observations (found in the column labeled “Exp. AccV Coeff.”) were significantly lower than this. Experimental values for the accelerating voltage coefficient ranged from 0.3 – 0.9 (with one exception of 1.9). This means that both models overpredict the importance of accelerating voltage to CD shrinkage, a serious modeling flaw. Future studies could be directed at resolving this accelerating voltage discrepancy.

3.6 Investigation of the film shrinkage mechanism

The models in this paper assume that CD shrinkage is in essence caused by an undefined film shrinkage mechanism that occurs during electron penetration. Attempts were made to understand the cause(s) of the film shrinkage.

Several e-beam cured samples of AR237J were measured on a Magna-IR 760 (FTIR; see Figure 6). Note the disappearance of both the 1725 and 1800 cm^{-1} peaks, corresponding to the carbonyl region. The peak signatures of AR237J during exposure to electron cure are practically identical to previously published peak signatures for PAR-705.[3]

The mass loss during e-beam cure was analyzed with a Stanford Research RGA200 (Residual Gas Analyzer; see Figure 7). Most of the volatiles observed had < 45amus. Guesses were made that the peak at 44amu might correspond to carbon dioxide, the peak at 28amu possibly corresponding to both nitrogen and carbon monoxide. If the peaks at 28 and 44amu do in fact contain carbon monoxide and dioxide, perhaps these are the volatile products of the carbonyl-loss reaction.

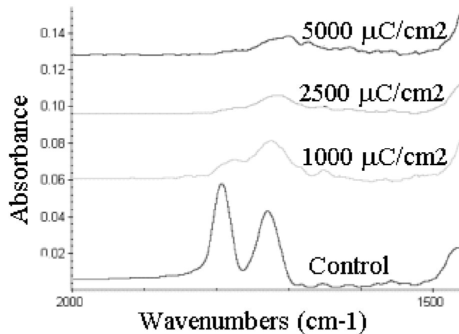


Figure 6: FTIR traces of AR237J during e-beam cure

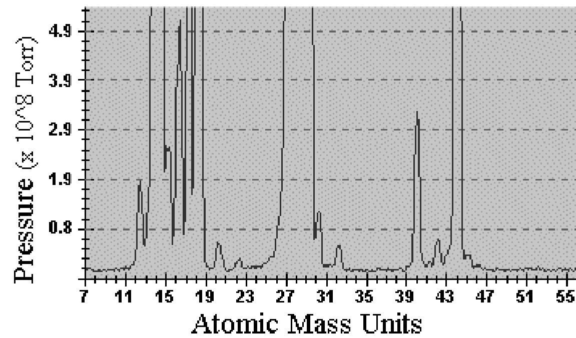


Figure 7: RGA traces of AR237J during e-beam cure

We were curious to see if the film shrinkage mechanism was related to heat. Wafers were coated with AR237J, given various e-beam cure doses (0-5000μC/cm^2), and then subsequently thermally baked for 60s at various temperatures (60-210C). After each e-beam cured sample was thermally baked, the film shrinkage amount was roughly the same (22-32%) for all doses of e-beam curing. This suggests that the e-beam cure shrinkage mechanism may be a thermal mechanism, possibly a thermal decomposition between 180 and 210C.

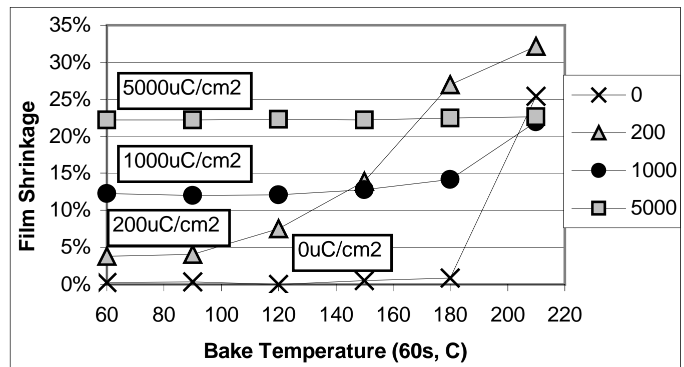


Figure 8: Film shrinkage of AR237J vs. e-beam cure dose and thermal bake

This thermal decomposition temperature (180-210C) roughly matches a paper study estimate of the heat produced at each SEM pixel during measurement. A 0.5keV beam was estimated to potentially raise the sidewall photoresist temperature as much as 400C during each measurement. Many assumptions are used in this estimate, and it is unknown if thermal diffusion would substantially lower this temperature increase. Some of the paper study assumptions include: SEM current of 10pA, a beam diameter of 5nm, 5nm lateral penetration depth (a MC estimate), 5% of incoming beam energy goes into the sidewall as phonon excitation (a MC estimate), 0.1μs pixel dwell time / repetition, 16 repetitions / pixel location, and a heat capacity for photoresist of 1 J/g °K.

4. CONCLUSION

Two linewidth shrinkage models are proposed, as an alternative to the three-term exponential decay fitting function. Both models offer valuable relationships between physical properties and CD shrinkage profiles through assumptions of electron behavior in photoresist. Both models predict the same CD shrinkage amplitudes. The primary difference between the models lies in their estimate of time constants (how many measurements are needed to fully shrink the CD). The Multi-Dose model predicts that the SEM beam must strike the photoresist from three to seventeen times before the complete resist shrinkage mechanism has finished. Resist density was shown to remain relatively constant with electron cure dose (one of the assumptions for both models). While accelerating voltage is known to affect CD shrinkage, the models predict that CD shrinkage should be even more strongly modulated by accelerating voltage than experimentally observed. It is speculated that the resist shrinkage during SEM measurements is due to mass loss caused by a thermal decomposition reaction.

A portion of the 193nm lithography community is under the impression that improvements in SEM measurement conditions have minimized / eliminated the linewidth shrinkage effect. If this is true, our industry will happily focus on the numerous other challenges of the 193nm lithography node. However, one of three technological paths may be needed to combat the linewidth slimming issue if it persists. Path one involves resist chemists improving the e-beam stability of their formulations. Path two would involve the adoption of a measurement-preparation step, such as e-beam curing or equivalent technique. Path three would entail SEM manufacturers developing linewidth shrinkage algorithms capable of tracking the number of electron scans given to a sample and correcting the waveforms or CDs for each of these numerous scans to compensate for the shrinkage phenomenon. Models cannot in themselves fix the linewidth slimming issue, but the art of problem solving usually starts by understanding the problem.

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APPENDIX: SIMPLE SHRINKAGE MODEL EQUATIONS

Define α as film shrinkage coefficient and **d** as the lateral electron penetration depth

(A1) Single Resist/Air Interface Shrinkage(1st exposure only) = α d
(A2) Single Resist/Air Interface Shrinkage(2nd exposure only) = α [d – (1-α) d] = α^2 d
(A3) Single Resist/Air Interface Shrinkage(3rd exposure only) = α [d – (1+α)(1-α)d] = α^3 d
(A4) Single Resist/Air Interface Shrinkage(4th exposure only) = α [d – (1+α+α^2)(1-α)d] = α^4 d (…and so forth)

* Realize that a line CD contains two resist/air interfaces and thus has twice the magnitude of the Single Resist / Air Interface Shrinkages: (A5) Total CD Shrinkage = ΔCD = $2\sum_{i=1}^{meas}\alpha^i d$

* Realize that the formula in (A5) results in an exponential-decay response to CD shrinkage (when $\alpha < 1$).
Expand A5 and set it equivalent to exponential-decay response curve, introducing A (amplitude) and τ (time constant).

(A6) $\Delta CD = 2\sum_{i=1}^{meas}\alpha^i d = 2\alpha d + 2\alpha^2 d + 2\alpha^3 d + 2\alpha^4 d + \ldots + 2\alpha^{meas} d = A\left[1-e^{-meas/\tau}\right]$

* Divide both sides by $2\alpha d$: (A7) $1 + \alpha + \alpha^2 + \alpha^3 + \ldots + \alpha^{meas-1} = \frac{A}{2\alpha d}\left[1-e^{-meas/\tau}\right]$

* Realize that for an infinite geometric series, $\sum_{i=0}^{\infty} ar^i = a + ar + ar^2 + \ldots = \frac{a}{1-r}$ for $0 < r < 1$.

* When the number of measurements approaches infinity,

(A8) $1 + \alpha + \alpha^2 + \alpha^3 + \ldots = \frac{1}{1-\alpha} = \frac{A}{2\alpha d}$ (A9) $A = \frac{2\alpha d}{1-\alpha}$

* Substituting (A9) into (A7): (A10) $(1-\alpha)(1 + \alpha + \alpha^2 + \alpha^3 + \ldots + \alpha^{meas-1}) = 1-e^{-meas/\tau}$

(A11) $\alpha^{meas} = e^{-meas/\tau}$ (A12) $\ln \alpha^{meas} = -meas/\tau$ (A13) $\tau = -\frac{1}{\ln \alpha}$

(A14) $\alpha = e^{-1/\tau}$ (A15) $d = A\frac{1-\alpha}{2\alpha}$

MULTI-DOSE MODEL EQUATIONS

Define α_i as film shrinkage coefficient for resist during its **i**th exposure, β as shrinkage decay constant, $\mathbf{r_{i,j}}$ as the depth of resist with ***i*** (*i* = 0,1,2…) exposures prior to the ***jth*** (*j* = 1,2,3…) measurement, $\mathbf{s_{ij}}$ as the shrinkage from resist with ***i*** exposures after the ***jth*** measurement, and **d** as the lateral electron penetration depth.

(A16) $\alpha_2 = \alpha_1 \beta$ (A17) $\alpha_3 = \alpha_2 \beta = \alpha_1 \beta^2$ (A18) $\alpha_i = \alpha_{i-1} \beta = \alpha_1 \beta^{i-1}$

(A19) $r_{ij} = (1-\alpha_i)\, r_{(i-1)(j-1)} = (1-\alpha_1 \beta^{i-1})\, r_{(i-1)(j-1)}$

(A20) $d = \sum_{i=0}^{\infty} r_{ij}$ (A21) $r_{0j} = d - \sum_{i=1}^{\infty} r_{ij}$ (unexp. resist depth = penetration range – exp. resist depth)

* Realize a boundary condition: $r_{i1} = 0$ for all i (no photoresist exposed prior to 1st measurement)

(A22) $s_{ij} = \alpha_i\, r_{(i-1)j} = \alpha_1 \beta^{i-1} r_{(i-1)j}$

(A23) $\Delta CD = 2\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} s_{ij}$ (factor of 2 due to line CD containing two resist/air interfaces)

(A24) Total % Film Thickness remaining after infinite number of exposures = $\prod_{i=1}^{\infty}(1-\alpha_i) = \prod_{i=1}^{\infty}(1-\alpha_1\beta^{i-1})$

(A25) Total % Film Shrinkage after infinite number of exposures = $\alpha_{total} = 1-\prod_{i=1}^{\infty}(1-\alpha_i) = 1-\prod_{i=1}^{\infty}(1-\alpha_1\beta^{i-1})$