Determining Free Volume Changes During the PEB and PAB of a Chemically Amplified Resist

Sean D. Burns[a], Michael D. Stewart[a], James N. Hilfiker[b], Ron A. Synowicki[b], Gerard M. Schmid[a], Colin Brodsky[a], and C. Grant Willson[a]

[a]Department of Chemical Engineering, University of Texas at Austin, Austin TX 78712
[b]J.A. Woollam Co., Inc. 645 M St. Suite 102, Lincoln, NE 68508

Chemically amplified resists provide some trade-off between resolution and amplification. While it is necessary for a single photogenerated acid to be mobile enough to cause several deprotection reactions, this inevitably leads to some linewidth spread. An acid molecule mobile enough to travel to several reaction sites is also mobile enough to move into unexposed regions of the resist. In order to optimize this trade off and design better photoresists, it is necessary to gain a complete understanding of the mechanism of acid transport during the post exposure bake. Some proposed mechanisms for acid transport consider the transport to be reaction enhanced in some way. The reaction front propagation model suggests that the deprotection reaction enhances local acid transport by either the generation of free volume or the plasticization of the resist by the reaction by-products. As the volatile reaction byproducts leave the resist, the free (or plasticized) volume collapses, providing a mechanism to halt acid transport. However, direct experimental evidence has not yet been provided to establish that free volume is indeed generated during the post exposure bake (PEB).

The purpose of this work is to experimentally investigate free volume changes during the PEB. One method for investigating the density (free volume) change is to measure the index of refraction changes during the PEB. A real time spectroscopic ellipsometer at J.A. Woollam Co. was used to monitor the index of refraction of t-BOC protected poly(4-hydroxystyrene). Another method for investigating both plasticization and free volume changes is to simultaneously monitor the reaction kinetics and the relaxation of the polymer. The kinetics of the reaction were monitored in real time by FTIR spectroscopy while the film thickness change was measured simultaneously with multiwavelength interferometry. The results of these analyses indicate that bulk free volume changes during the PEB are small. Furthermore, a nitrogen purge over the t-BOC film was found to drastically change the rate of reaction. The cause of this phenomenon was investigated by varying the purge rate, purge gas and by monitoring the rate of water sorption by quartz crystal microbalance (QCM). The humidity of the purge stream strongly affects the reaction kinetics.

The IR/interferometry technique was also used to measure free volume changes during the post apply bake (PAB) of novolac and polyhydroxystyrene films. The free volume changes during the PAB were also found to be small. This technique was also used to determine the volume fraction of residual solvent during the PAB.

Keywords: acid diffusion, free volume, post exposure bake, post apply bake, water sorption

Introduction

Linewidth spread encountered in chemically amplified (CA) resists is generally attributed to unwanted acid transport into unexposed areas of the resist during the post exposure bake (PEB)[2]. As the size of printed features shrink, the importance of this intrinsic bias grows. A complete understanding of acid reaction and transport is important for modeling and improving the lithographic process, as well as for designing better resists. The deprotection reaction of a common chemically amplified resist system is shown in Figure 1. This is the acid catalyzed reaction of poly(t-butyloxycarbonyloxystyrene) (t-BOC) to poly(4-hydroxystyrene) (PHOST). The kinetics of this reaction have been studied previously by Wallraff *et al.*[3] Ito *et al* have shown that this reaction is somewhat more complex than previously thought,[4] but for the purposes of this work it is assumed that the simple reaction scheme shown in Figure 1 is operative. The acid transport mechanism has also been studied in many ways and is a topic of much discussion in the literature. Early work on the subject attributes acid transport to Fickian diffusion,[5,6] and some work has been done to model the PEB using a reaction-enhanced diffusion mechanism.[7] Many researchers have incorporated free volume concepts into their study and/or analysis of acid transport[7-9,15-16] and some modeling has been done incorporating concentration dependent diffusion coefficients.[9]

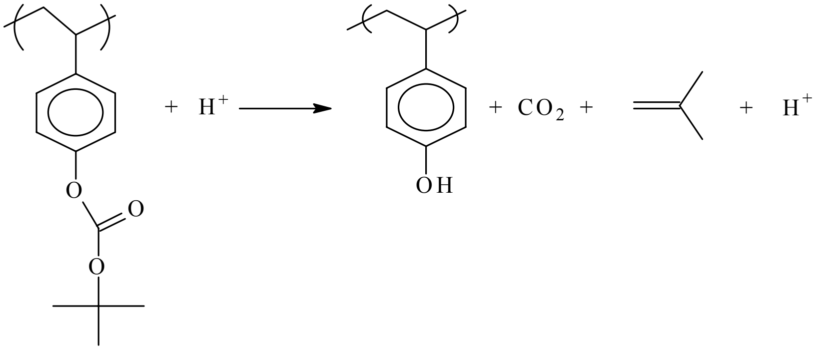

Figure 1. Acid Catalyzed Deprotection of poly(t-BOC styrene)

Hinsberg *et al* have taken an approach that does not involve free volume concepts. They developed a model that rigorously considers the kinetics of the deprotection reaction, and separately allows Fickian acid diffusion.[10,11] Their model captures the non-Fickian nature of acid transport by assigning a different acid diffusion coefficient to the initial (t-BOC) and final (PHOST) materials. Their analysis leads to acid diffusion lengths on the order of ~5 nm during typical PEB (100^{o}C for 120 sec). Linewidth spread is attributed mainly to the long catalytic chain length of the acid molecules.[10,11]

Our research group has proposed a reaction front model for acid transport.[12,13] The premise of the reaction front model is that as the deprotection reaction takes place, a transient enhancement of local acid transport occurs. The mechanism for this enhancement could be either free volume, plasticization, or heat given off by the exothermic reaction. Free volume and plasticization are known to increase the mobility of penetrant molecules within a polymer film.[14] Relaxation of the polymer depletes this free volume, such that after some time the acid molecules are essentially trapped (the diffusion coefficient is less than 10^{-8} $\mu m^2/s$).[12] A diagram that describes the general premise of this model is shown in Figure 2. Another possible reaction enhanced transport mechanism is that the exothermic deprotection reaction temporarily raises the film locally to near or above its T_g, thus providing temporary enhanced mobility. This mechanism is not explored in this work.

There may be other effects that the previous discussion does not address. For example, if one considers a hypothetical non-reactive t-BOC film, the diffusivity of a typical acid molecule may be significantly different in the t-BOC film than in a PHOST film due to its lower Tg and differences in dielectric constant and density between the two materials. Either of these effects may help explain faster

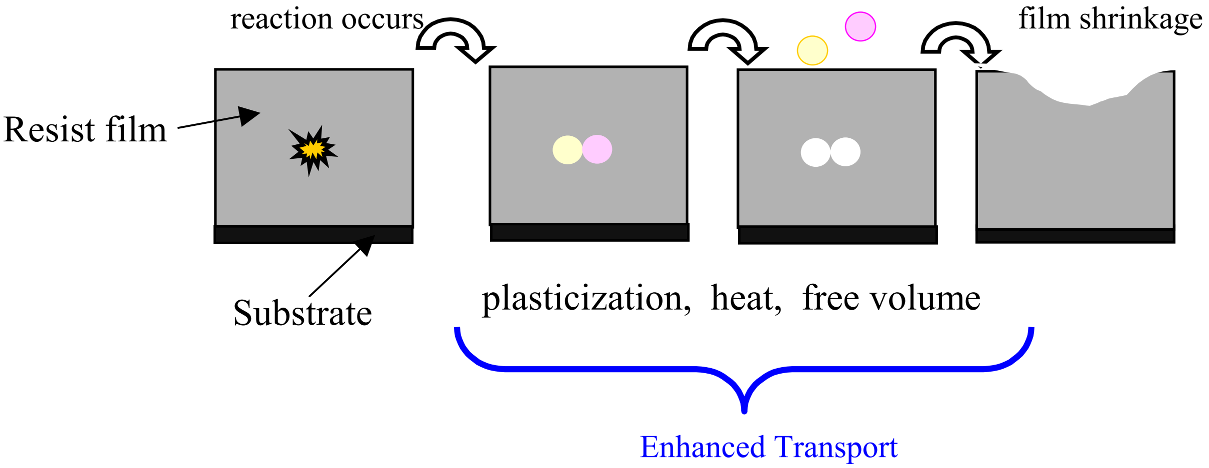

Figure 2. Diagram of Reaction Enhanced Transport

transport through t-BOC.[11,12] It should be noted that the term "acid transport" describes the simultaneous movement of both a proton and its bulky counterion. Shi has calculated that the attraction between a proton and its counterion is so large that they always remain close together with the Debye length calculated to be about 1 nm.[17] Experimentally, it is observed that the size of the PAG counterion has a large influence upon acid transport, in agreement with Shi's calculations.[18]

In this work, the evolution of free volume was investigated with two methods. The first technique involved monitoring the index of refraction of the resist film with a real time spectroscopic ellipsometer during the PEB. The second technique involved simultaneously measuring the kinetics of the deprotection reaction and the film thickness change during the PEB. The reaction kinetics were monitored by Fourier transform infrared spectroscopy (FTIR) and the film thickness change was monitored by multiwavelength interferometry (MWI). It is well known that the deprotection reaction results in a significant thickness change of the polymer film,[10] but exactly *when* this thickness change occurs relative to the reaction has not been studied. The simultaneous measurement of reaction kinetics and film shrinkage provides useful information about the concentration of reaction byproducts and void volume during the post exposure bake.

Unfortunately, reflectance interferometry requires the assumption that the index of refraction of the film is constant during the PEB. For a reacting film, this may be a poor assumption. However, it was possible to correlate the index of refraction data (from the spectroscopic ellipsometer) with the MWI data in order to determine the correct thickness change with interferometry.

During the course of these experiments and in discussion with colleagues,[19] the nitrogen purge was found to have a significant influence on the deprotection reaction rate of t-BOC. This phenomenon was investigated by monitoring the effects of purging a t-BOC resist with nitrogen, dry air, and nitrogen bubbled through water. Upon finding that humidity in the purge stream had a strong effect on the reaction kinetics, the rate of sorption of water in t-BOC and PHOST films was studied with a QCM system.

Materials and Experimental

The photoresist used, consisted of fully t-BOC protected poly(p-hydroxystyrene) that was synthesized by free radical polymerization of t-butyloxycarbonyloxystyrene monomer from Triquest Chemical Co. The casting solvent used was propyleneglycol methyl ether acetate (PGMEA), purchased from Aldrich Chemical Co. and used as received. The photoacid generator (PAG) was bis(p-tert-butylphenyl)iodonium perfluorobutanesulfonate, provided by Midori Kagaku Co. The resist formulation consisted of 20 wt% solids, of which 2.5% was PAG. The resists were spun at 2500 rpm for 30 seconds, and post apply baked at 90°C for 90 seconds to provide approximately 1.4 µm films. The films were exposed with 100 mJ/cm^2 of broadband light with a JBA high performance collimated UV light source. The delay time between exposure and PEB was less than 5 minutes for all experiments.

Cresol novolac from Schenectady International (MW=9370, Pd=4.9) and poly(4- hydroxystyrene) from Hoechst Celanese (MW=29,700, Pd=1.11) were used in the PAB studies over a temperature range of 70-110°C. PGMEA was used as the casting solvent. Films of each resin were spin coated between 1.5-2.0 μm thick. The post apply bake was monitored with both FTIR and interferometry (described below). There was a constant 2 minute delay between spin coating and baking.

An M-2000® spectroscopic ellipsometer at the J.A. Woollam Co. was used to monitor the PEB at 90°C. The film was heated with an OMEGA silicone rubber 3" circular heating pad, controlled with a Staco Co. Variac.

The disappearance of the t-BOC carbonyl peak was monitored by real time FTIR spectroscopy during the post exposure bake (PEB). A Nicolet Magna 550 FT-IR with an attached liquid nitrogen cooled MCT/B external IR detector from Axiom Analytical was used to collect sample spectra from wafers that were placed on a temperature controlled hotplate under a nitrogen purged sample chamber. A salt disk was placed in the IR chamber to block the nitrogen purge from reaching the sample, keeping the environment the same at both points of interrogation. FTIR spectra were collected every 0.5 second. The thickness change was monitored in real time with a multiwavelength interferometer (MWI). The details of this system are described elsewhere.[20] Thickness measurements were made every 0.25 seconds. The FTIR and MWI interrogation beams were approximately 1 inch apart on the hotplate. The temperature difference between these two points was measured to be less than 1°C. The PEB was monitored in this manner over a temperature range of 80-95°C. (Data at lower temperatures is also published by researchers at IBM.[21]) A diagram of this apparatus is shown in Figure 4. The same apparatus/technique was used to monitor the PAB of novolac and PHOST. The FTIR was used to monitor the change in the carbonyl peak of PGMEA as it evolved from the resist film during the post apply bake.

The rate of deprotection of t-BOC during the PEB was monitored at several purge rates by varying the flow of nitrogen through the FTIR. In a separate experiment, the thickness change was monitored simultaneously at a control spot (ambient conditions) and under a gas purge that was simply blown onto the film. The gas used for the purge was varied. Industrial grade nitrogen and air were purchased from PraxAir and dry air (less than 3 ppm water) was purchased from Air Liquide. The flow rate of the purge was kept constant at 45 ml/s for these experiments.

The rate of sorption of water into both t-BOC and PHOST films was determined by simultaneous QCM measurements. The details of the QCM system are described elsewhere.[22] Two t-BOC films (exposed and unexposed) were loaded into the sample chamber. The chamber was heated to 70°C while pulling vacuum. The system equilibrated for about 4 hours, allowing the exposed film to completely deprotect into PHOST. Water vapor at 20% humidity was then introduced into the sample chamber, and the frequency shift (mass uptake) of the films were monitored by the QCM over time.

Results and Discussion

The change in index of refraction at 633 nm over time for a t-BOC film at 90°C is shown in Figure 3. The index of refraction of the initial film is approximately 1.5. During the beginning of the bake, the index decreases by about 0.005. Then, the index increases almost linearly to the final value of 1.54. The index of refraction is dependent upon both composition and density, but in this case the assumption is made that it correlates mainly with density. This is in agreement with the higher density of PHOST. Furthermore, the results indicate that the density never decreases substantially, providing evidence that free volume does not increase substantially during the PEB. The small decrease at the beginning may be due in part to thermal expansion of the film at the beginning of the bake as discussed below.

The simultaneous kinetics/thickness experiments are shown in Figure 5 at PEB temperatures of 80 and 95°C. The dark lines show the change in the integrated carbonyl peak with time (the reaction kinetics).

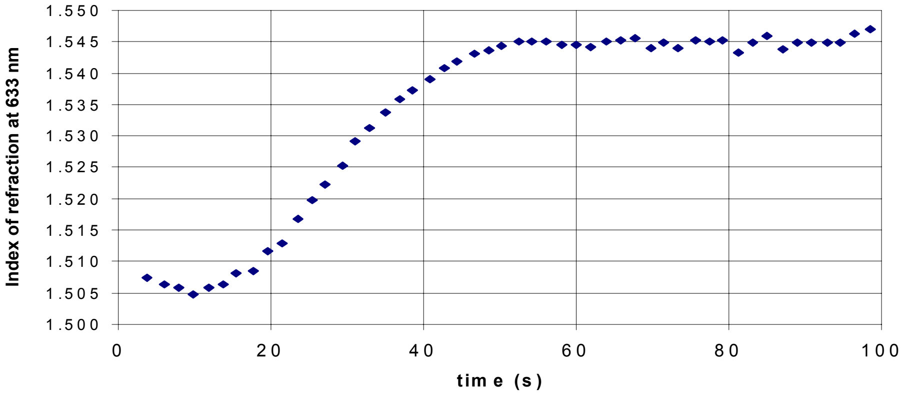

Figure 3. Index of Refraction during 90°C PEB monitored by a real time spectroscopic ellipsometer

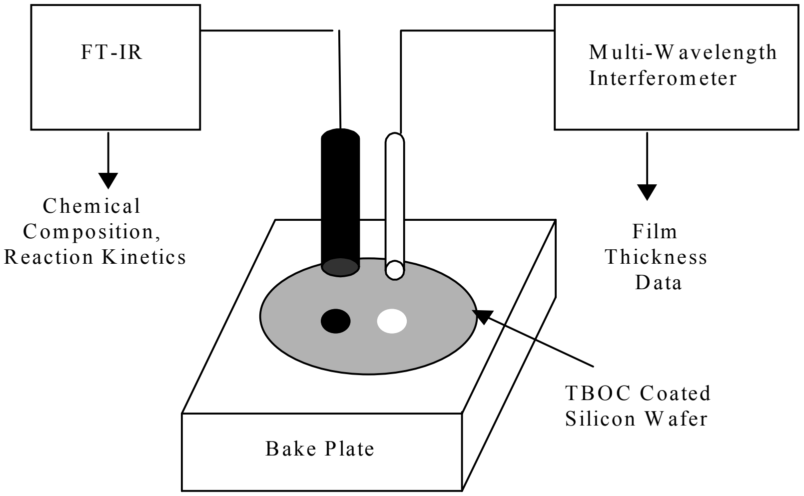

Figure 4. Diagram of Simultaneous FTIR/Interferometry Technique

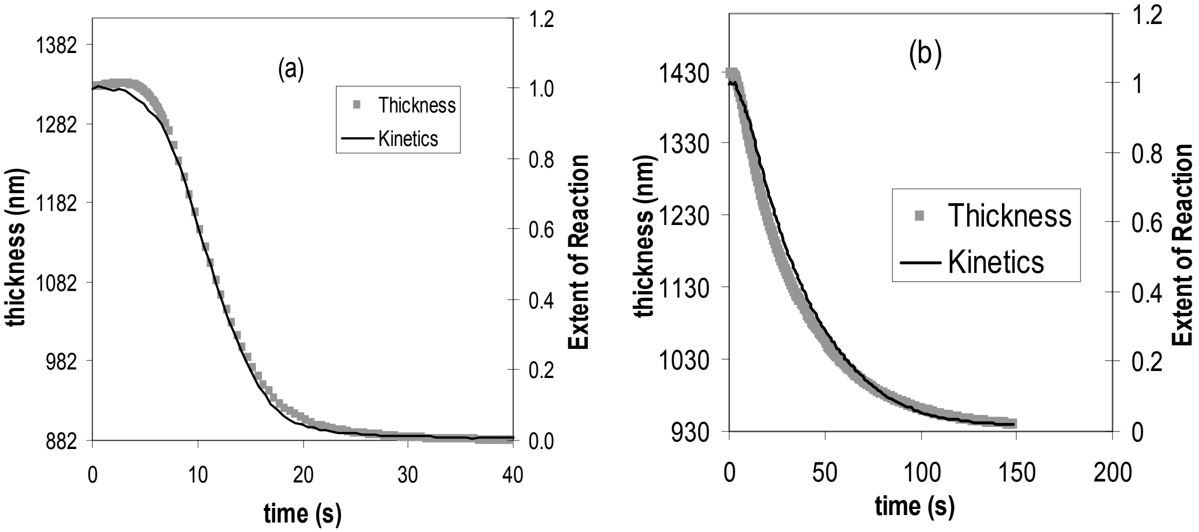

Figure 5. Results of Simultaneous Kinetics/Thickness Measurements During PEB at (a) 95°C, (b) 80°C

These data have been normalized such that the fraction of t-BOC remaining is shown at time *t*. The gray lines show the relaxation of the polymer (the thickness data). These data are presented as an absolute thickness change in nm. The y-axis has been adjusted such that the initial thickness corresponds to that of the initially protected polymer and the final thickness corresponds to the completely deprotected polymer. The kinetics and the thickness change are nearly indistinguishable in both experiments. At 95°C, there is a slight increase in the film thickness at the beginning of the reaction. The thickness increase corresponds well to the slight decrease in the index of refraction at the beginning of the bake. This thickness increase and decrease in density may be due to thermal expansion of the film as the temperature ramps from room temperature to above 90°C, or the thickness increase may indicate a slight increase in free volume due to the deprotection reaction. Separating the two effects will be dealt with in future work. Overall, the results of these experiments indicate that the multiple steps shown in Figure 2 all occur very quickly. That is, carbon dioxide and isobutylene leave the film quickly, *and* the polymer relaxes very quickly. For this bulk experiment, there is no observable increase in the concentration of gaseous byproducts and/or free volume. Hinsberg *et al* report similar results.[21] It is possible that the reaction byproducts locally enhance diffusion of acid (an effect that cannot be easily observed). It is also possible that the exothermic reaction heats the film locally, providing another possible mechanism for transient enhancement of acid diffusion.

While there is no observable increase in free volume, the increase necessary for enhanced diffusion need not be large. Most models that relate diffusivity to free volume are exponential in nature. For example, the Fujita-Doolittle model[26] predicts an increase in the diffusion coefficient by as much as four orders of magnitude (using reasonable parameters) with as little as 2% increase in free volume. The resolution of the FTIR/MWI experiment may not be adequate enough to detect such a small increase in free volume. Future work will involve improvements in the resolution of the experiment and determining the correct parameters for use in the Fujita-Doolittle model.

The Effect of Nitrogen Purge on Deprotection Kinetics

The deprotection kinetics of t-BOC were monitored at several different flow rates of the nitrogen purge. The results are shown in Figure 6. Between 27 and 50 ml/s, the rate of reaction was the same. At 0 ml/s (the purge was blocked with a salt disk) the rate of reaction was drastically different. The rate of reaction was considerably slower, a rather unexpected result. One might predict that the nitrogen purge would cool the film, resulting in slower kinetics at a higher flow rate, but the opposite effect was observed.

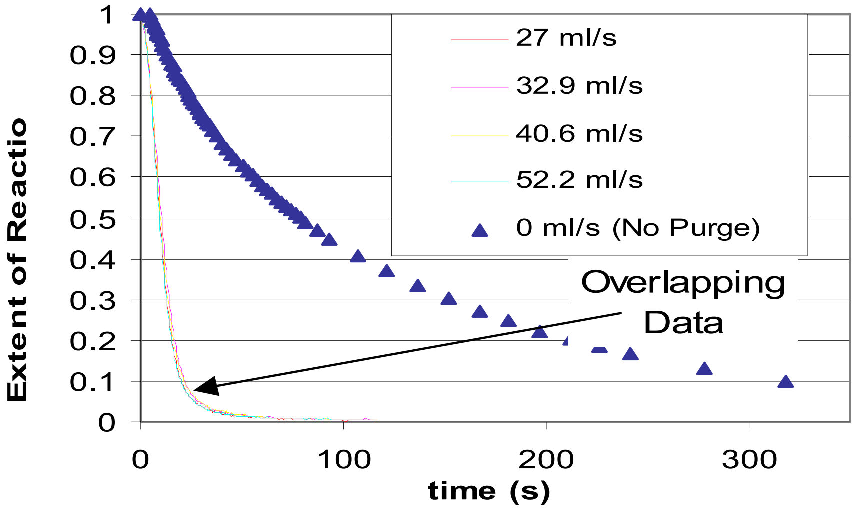

Figure 6. Rate of t-BOC Deprotection at Various N_2 Flow Rates (70°C PEB)

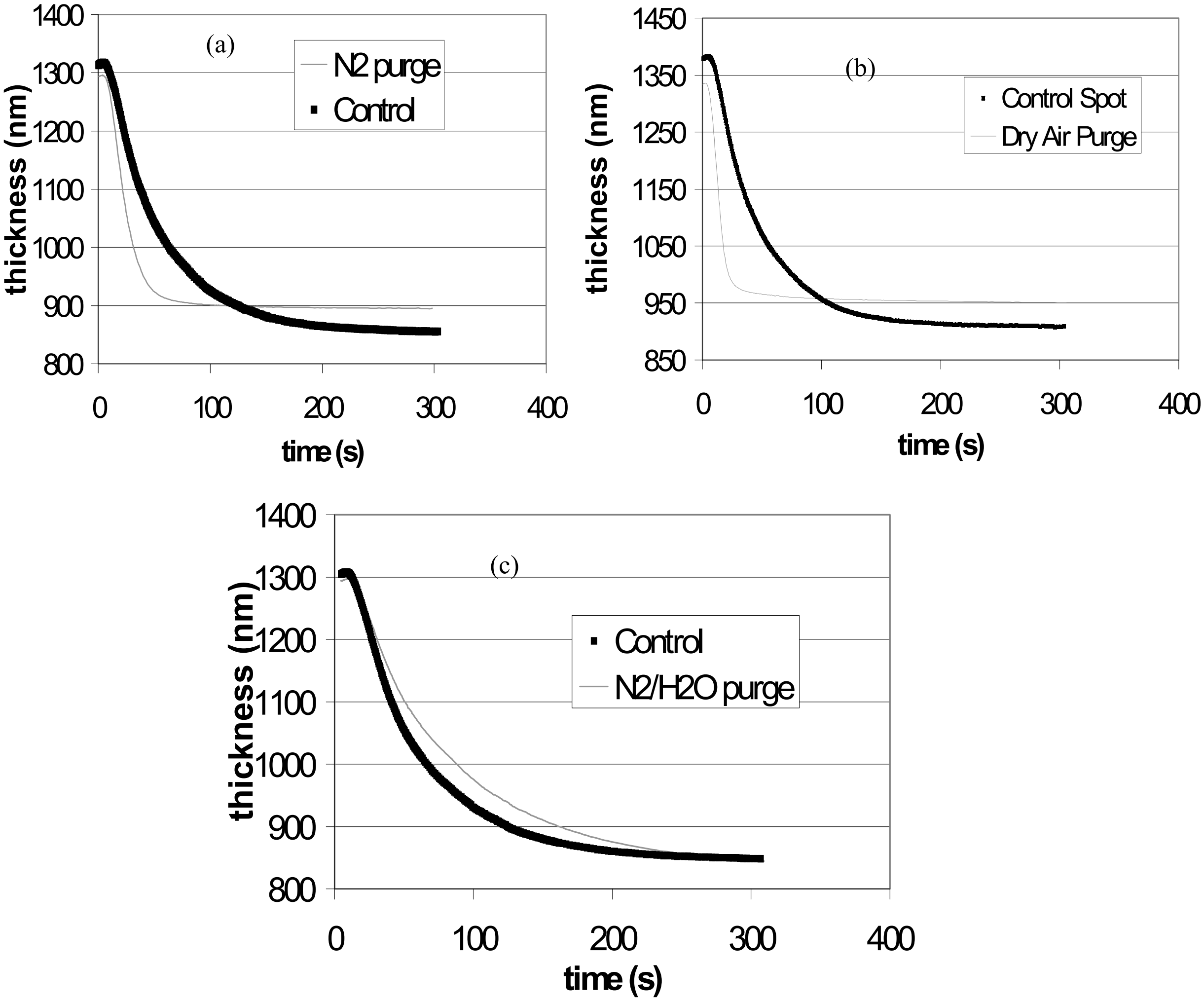

Figure 7. Thickness Change During 80°C PEB with Various Purge Gases: (a) Nitrogen,(b) Dry Air, (c) Nitrogen bubbled through water.

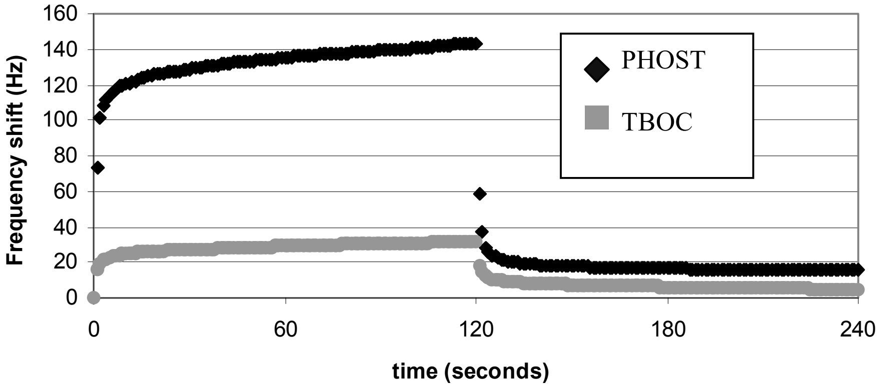

Figure 8. Water Vapor Sorption into t-BOC and PHOST at 70°C, 20% Humidity, Followed by Evacuation at 120 seconds

Two general hypotheses were considered.[19] First, mass transport effects could influence the evolution of byproducts, resulting in a Le-Chatelier effect upon kinetics. Alternatively, environmental contamination could affect the reaction in an unknown way. Since the reaction rate was constant over such a wide range of flow rates, the latter hypothesis was considered to be more viable. This hypothesis was tested by examining the effects of purging the resist under various gases. The results of these experiments at a PEB temperature of 80°C are shown in Figure 7.

Under a nitrogen purge, the thickness change over time was considerably faster than the same film under ambient conditions. The same effect was observed using dry air as the purge gas, thus eliminating oxygen as a possible contaminant. However, when nitrogen is bubbled through water, the opposite effect was observed. That is, the thickness change occurs slower than under ambient conditions. Thus, humidity in the purge stream has a significant effect on the reaction kinetics. For water vapor in the environment above the film to affect the rate of reaction within the film, considerably fast transport of water must occur. Our hypothesis is that water has a higher affinity for polyhydroxystyrene than t-BOC (since PHOST is more polar) and that the sorption of water into PHOST occurs very quickly during the PEB. As the deprotection reaction occurs, water from the atmosphere (if available) sorbs into the resist film, lowering the pKa of some acid molecules and slowing the overall rate of reaction. If the film is purged during the PEB with a dry gas, there is no water available and thus the reaction is not slowed.

Sorption of Water into t-BOC and PHOST Films

This hypothesis was tested by measuring the rate of sorption of water into both t-BOC and PHOST films at 70°C. The results of this experiment are shown in Figure 8. The results are plotted as frequency shift of the QCM crystal versus time. The mass uptake of water in the PHOST film was over four times as large as the mass uptake of water in the t-BOC film. The frequency shift shown for PHOST corresponds to ~1-2 wt% of the film. More importantly, the sorption of water was fast, with a large portion of water sorbing into the films in the first few seconds of exposure. This confirms the hypothesis that water has a higher affinity for PHOST, and that water sorption is fast. At 120 seconds, vacuum was applied to the QCM chamber. A small amount of water remained in both the PHOST and t-BOC films, but the mass of water in the PHOST film remained larger, further demonstrating that water has a higher affinity for PHOST.

The hypothesis of base quenching by water from the atmosphere appears to be viable, but is probably an oversimplification of the phenomenon. For example, the final film thickness is lower when no gas purge is used during the PEB (Figure 7). This was found to be a highly reproducible trend both in our lab and at IBM.[21] In both cases (purge or no purge), the IR data clearly shows that the reaction has gone to completion (by the absence of the carbonyl peak), but in the case of a gas purge, it is clear that additional mass remains in the film. The alternate reaction pathways discussed by Ito[4] may be occurring in different proportions. Significantly different peak heights of the C-H stretch in the IR spectra after a PEB with varying purge rates have been reported.[21] Apparently, different chemistry occurs at various flow rates of the nitrogen purge, which may or may not be related to water sorption. This remains an interesting topic for future study.

Determining Free Volume Changes During PAB

The post apply bake was also monitored using simultaneous FTIR and interferometry. A typical result is shown in Figure 9 for novolac spun cast from PGMEA at a bake temperature of 70°C. The absolute thickness data is reported on the left y-axis, and the normalized carbonyl peak area is reported on the right y-axis. The right y-axis was adjusted such that the initial and final values of thickness and carbonyl peak correspond. It should be noted that the thickness data shown in Figures 9-11 have not been corrected for changes in index of refraction. Cauchy coefficients were used that were determined after a 90 second PAB, over a temperature range of 70-110°C. Thus, the largest error in thickness is during the first 50 seconds of the bake. It is estimated that the maximum error in the absolute thickness is under 3%.

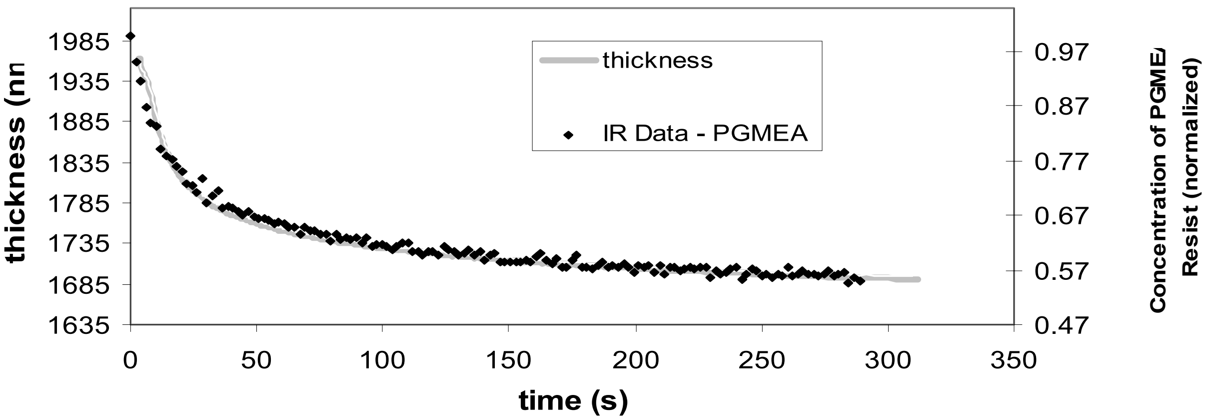

Figure 9. Simultaneous FTIR/Thickness Measurement During 70°C PAB (Novolac/PGMEA)

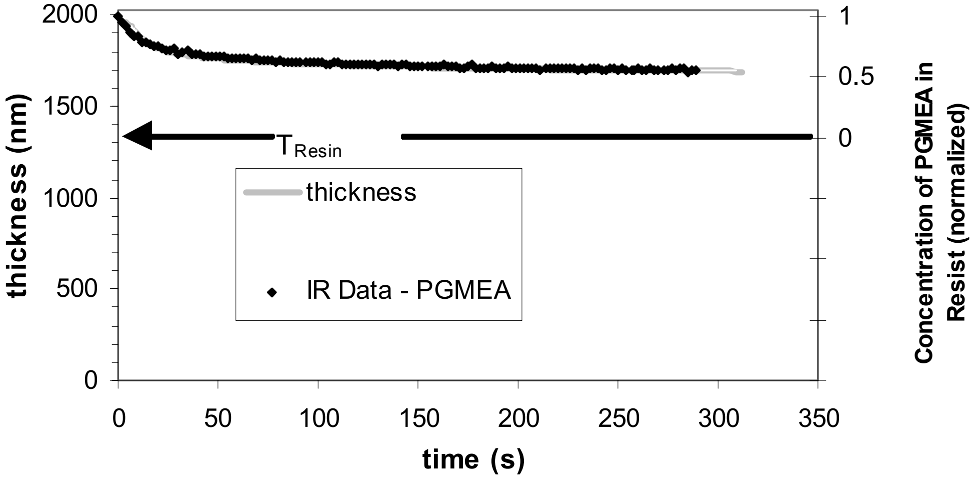

Figure 10. Expanded View of Figure 9

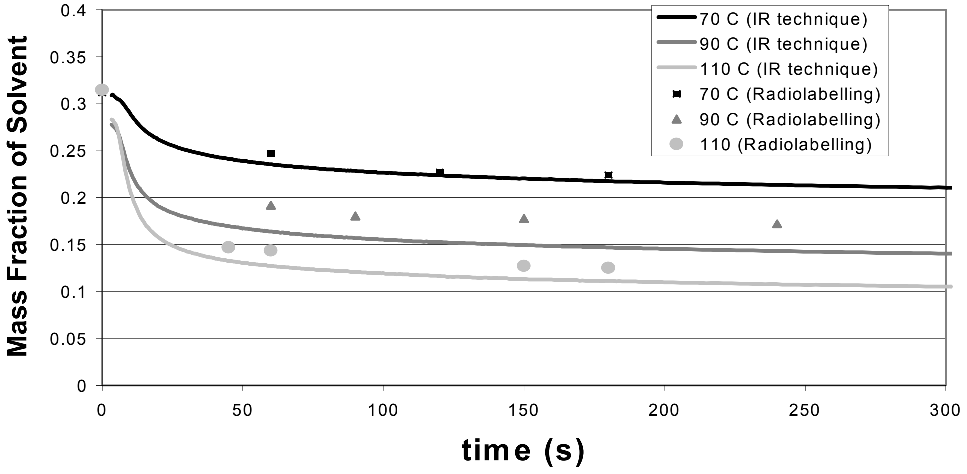

Figure 11. Comparison of PGMEA mass fraction Obtained from Radio-labeling and from FTIR/Thickness Measurements

However, the relationship between solvent content and index of refraction has been reported to be linear,[27] and the relationship between index and the calculated thickness is linear.[20] Thus, the error in thickness throughout the bake is linear, and since the IR data is scaled linearly to match the thickness, the IR data will "match" the thickness data regardless of whether or not the index of refraction changes are accounted for.

Since PGMEA evolves from the film at the same rate that the thickness decreases, the thickness change during the PAB can be attributed mainly to the evolution of solvent. Thus, the intrinsic free volume of the polymer film effectively remains constant during the PAB. This assumption was made in the PAB model of Mack[23] and our results confirm that the assumption is valid. The data shown in Figure 9 are typical of both novolac and PHOST cast from PGMEA over a range of bake temperatures of 70-110°C.

It is possible to glean even more information from this experiment. Figure 10 shows the same data as Figure 9 with an expanded axis. It is evident from Figure 10 that it is possible to attribute the entire amount of residual solvent in the film to a volume element at any time during the bake. For example, a loss of half of the initial solvent corresponds to a thickness decrease of ~300 nm (or 15% of the total film volume). In the hypothetical case of an infinite bake, in which all the solvent evolves, the thickness of the dry film would be ~1300 nm (a loss of ~30% of the total film volume). The thickness that corresponds to zero concentration of solvent is labeled T_{resin}. This analysis suggests that the volume fraction of solvent in the film can be determined at any time *t* by the following equation:

$$\phi_{solvent} = \frac{T(t) - T_{resin}}{T(t)} \tag{1}$$

where $\phi_{solvent}$ is the volume fraction of solvent, T(t) is the overall thickness at time *t*, and T_{resin} is defined above. The volume fraction of PGMEA in novolac resin was calculated using the Equation (1) at bake temperatures ranging from 70-110°C. The weight percent of residual PGMEA has previously been determined for the same novolac resin over the same PAB temperature range for various bake times by a radiolabeling technique[24]. The calculated volume fraction was converted to a mass fraction using an approximation by Mack[25] for comparison purposes. The radio-labeled data and the data determined by this technique are shown in Figure 11. The data correlate quite well. This technique provides a good approximation to the concentration of residual casting solvent within a film. It agrees well with radio-labeling techniques, but it has the advantage of being much easier. Other advantages are that it is nondestructive, and it is only necessary to coat one wafer per bake temperature. The major drawback is

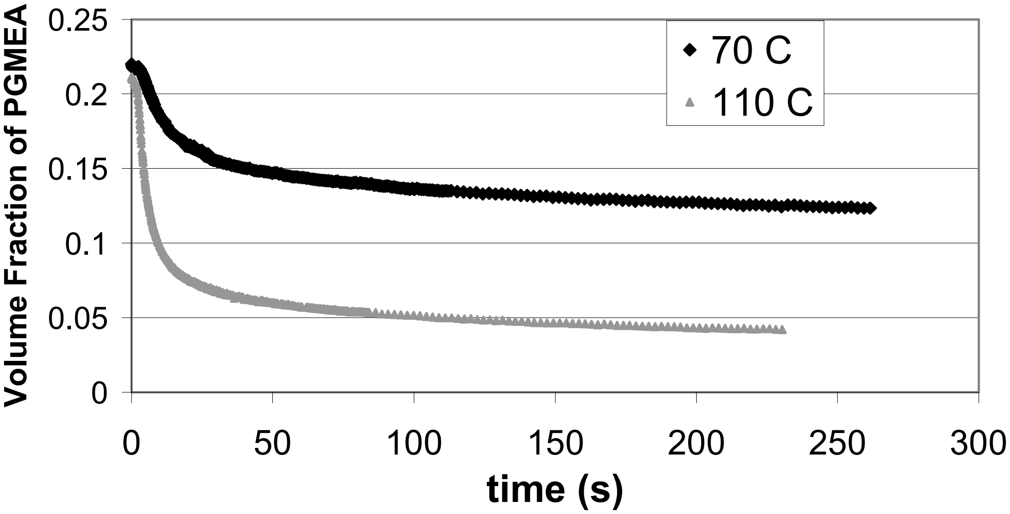

Figure 12. Volume Fraction of PGMEA in PHOST determined by Equation (1)

that it can only be used for resists in which the casting solvent has a unique IR peak from the resin, e.g. it is not easy to monitor the concentration of PGMEA in a t-BOC film, as they both have a characteristic carbonyl peak. The volume fraction of residual PGMEA in PHOST is shown in Figure 12 at bake temperatures of 70 and 110°C.

Conclusions

A technique has been demonstrated to measure the free volume change during the PAB and PEB of photoresist films using simultaneous FTIR and reflectance interferometry. The free volume change during both PAB and PEB was small. The kinetics of t-BOC deprotection were shown to be dependent upon the purge gas over the resist. The proposed hypothesis is that sorption of water during the PEB leads to a lower pKa of the acid, and thus a slower reaction rate.

Acknowledgements

The authors wish to thank Bill Hinsberg and Greg Wallraff at IBM Almaden for sharing their results and for insightful discussions concerning the nitrogen purge phenomenon. The authors also wish to thank Chris Mack, Mark Smith, and Jeff Byers of Finle Technologies for several helpful discussions. We wish to acknowledge Midori Kagaku Co. for donating the PAG and Triquest Chemical Co. for donating t-BOC monomer. This research was supported by the Semiconductor Research Corporation (SRC contract # LC-460) and DARPA.

References

[1] Larry F. Thompson, C. Grant Willson, and Murray J. Bowden, *Introduction to Microlithography*, 2nd Edition, American Chemical Society, Washington D.C., 1994

[2] J. Sturtevant, S. Holmes, P. Rabidoux, *Proc. SPIE* **1672**, 114, (1992)

[3] G. Wallraff, J. Hutchinson, W. Hinsberg, F. Houle, P. Seidel, R. Johnson, and W. Oldham, *J. Vac. Sci. Technol.*, **12**, 3857 (1994)

[4] H. Ito and M. Sherwood, *Proc. SPIE* **3678**, 104 (1999)

[5] T. Fedenyshyn, J. Thackeray, J. Georger, M. Denison, *J. Vac. Sci. Technol. B.*, **12 (6)**, 1991

[6] L. Schlegel, T. Ueno, N. Hayashi, T. Iwayanagi, *Jpn. J. Appl. Phys.*, **11B**, 30,1991

[7] M.A. Zuniga and A.R. Neureuther, *J. Vac. Sci. Technol. B* **14**, 4221 (1996)

[8] L. Pain, C. Le Cornec, C. Rosilio, P.J. Panez*, Microelectronic Engineering* **30**, 271-274, 1996

[9] J.S. Petersen, C.A. Mack, J. Sturdevant, J.D. Byers, and D.A. Miller, *Proc. SPIE* **2438**, 167 (1995)

[10] G.M. Wallraff, W.D. Hinsberg, F.A. Houle, M. Morrison, C.E. Larson, M. Sanchez, J. Hoffnagle, P.J. Brock, G. Breyta, *Proc. SPIE* **3678**, 1999

[11] F.A. Houle, W.D. Hinsberg, M. Morrison, M.I. Sanchez, G. Wallraff, C. Larson, and J. Hoffnagle. *J. Vac. Sci. Tech. B* **18(4)**, 1874-1884, 2000

[12] S. V. Postnikov, M. D. Stewart, H. V. Tran, M. A. Nierode, D. R. Medeiros, T. Cao, J. B., S. E. Webber, C. Grant Willson *J. Vac. Sci. Technol. B.* , **17**, 3335-3338,1999

[13] M.D. Stewart, M.H. Somervell, H.V. Tran, S.V. Postnikov, C. G. Willson. Proc. SPIE **3999**, 665, 2000

[14] John J. Aklonis and William J. MacKnight, *Introduction to Polymer Viscosity 2nd Ed.*, 1982; Harry R. Allcock and Frederick W. Lampe*, Contemporary Polymer Chemistry 2nd Edition*, Prentice Hall, Englewood Cliffs, N.J., 1990

[15] E Croffie, M. Cheng, A. Neureuther, *J. Vac. Sci. Technol. B.*, **17**, 3339-3342,1999

[16] G. M. Schmid, V. K. Singh, L. W. Flanagin, M. D. Stewart, S. D. Burns, and C. Grant Willson, *Proc. SPIE* ***3999,*** 675, 2000

[17] X. Shi, *J. Vac. Sci. Tech. B* **17**, 350 (1999).

[18] T. Itani, H. Yoshino, M. Fujimoto, and K. Kasama, *J. Vac. Sci. Tech. B* **13(6)**, 3026-3029, 1995

[19] Private Communications with Dr. Bill Hinsberg and Dr. Greg Wallrath at IBM Almaden, October, 2000

[20] C.L. Henderson, *PhD Dissertation*, University of Texas at Austin, 1998

[21] W.D.Hinsberg,F.A.Houle,D.Pearson,M.I.Sanchez,H.Ito,J.Hoffnagle,"Real-Time Analysis of Volatiles Formed during Processing of a Chemically Amplified Resist" Located in these Proceedings

[22] C.J. Brodsky, H.F..Johnson,B.C.Trinque,A.T.Jamieson,C.G.Willson,"Graft Polymerization Lithography" Located in these Proceedings

[23] C.A. Mack, K.E. Mueller, A.B. Gardiner, J.P. Sagan, R.R. Dammel, and C.G. Willson, *J. Vac. Sci. Tech. B* **16(6)**, 3779-3783, 1998

[24] A.B. Gardiner et al, *Proc. SPIE*, **3049**, 850, 1997

[25] C. A. Mack, *PhD Dissertation*, University of Texas at Austin, 1998

[26] H.Fujita, A.Kishimoto, and K.Matsumoto, *Transactions of the Faraday Society*, Vol. **56**, 424-437, 1960

[27] S.Ficner,R.R.Dammel,Y.Perez,A.Gardiner, and C.G. Willson, *Proc. SPIE,* **3049**, 838, 1997