View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by University of Queensland eSpace

Non-CA Resists for 193 nm Immersion Lithography: Effects of Chemical Structure on Sensitivity

Idriss Blakey,[a] Lan Chen,[a] Yong-Keng Goh,[a] Kirsten Lawrie,[a] Ya-mi Chuang,[a] Emil Piscani,[b] Paul A. Zimmerman [b] and Andrew K. Whittaker[a] *

[a]The University of Queensland, Australian Institute for Bioengineering and Nanotechnology and Centre for Magnetic Resonance, St Lucia, Qld, Australia 4072; [b]Sematech 2706 Montopolis Drive Austin, Texas, USA, 78741

ABSTRACT

Initial studies are presented on the use of polysulfones as non-chemically amplified resists (non-CARs) for 193 nm immersion lithography. Polynorbornene sulfone films on silicon wafers have been irradiated with 193 nm photons in the absence of a photo-acid generator. Chemical contrast curves and contrast curves were obtained via spectroscopic ellipsometry and grazing angle – attenuated total reflectance FTIR spectroscopy. Results were consistent with previously reported mechanisms for the degradation of aliphatic polysulfones with ionizing radiation. It was shown that E0 values could be reduced significantly by using a post exposure bake step, which propagated depolymerization of the polymer. Initial patterning results down to 50 nm half pitch were demonstrated with EUV photons.

Keywords: Non-chemically amplified resists, non-CAR, 193 nm immersion lithography, polysulfone

1. INTRODUCTION

Chemically amplified resists (CARs) have been the work-horse of the semiconductor industry for many years. Typically, CARs for 193 nm lithography are comprised of a polymer that possesses pendant tertiary esters, a photo-acid generator (PAG) and a quencher. They rely on light being absorbed by the PAG, which then fragments to yield a strong acid along with other photodecomposition products. These strong acids catalytically deprotect the non-polar pendant tertiary esters to yield polar carboxylic acids. With a sufficient number of deprotection events this results in a switch in polarity of the polymer, such that it is soluble in an aqueous base. Hence, high contrast can be obtained between irradiated and non-irradiated portions of the wafer. A primary advantage of CARs is that because the process is catalytic, a single acid is able to deprotect many pendant groups, so that a single photon results in multiple deprotection events. However, this process occurs by diffusion, which at the length scales that are currently being patterned, result in image blur and line edge roughness. Diffusion of the acid has been arrested to some extent by the inclusion of base quenchers into photoresists, but even this solution is unlikely to be sufficient.

The issue of line edge roughness has led to the reinvestigation of non-chemically amplified resists [1], which have previously been studied [2, 3] prior to the advent of CARs. This class of polymer resist relies on the absorption of light by the polymer, which then results in a chain scission event. After a sufficient number of scission events, the solubility of the polymer increases, resulting in contrast being obtained between irradiated and un-irradiated portions of a wafer. As opposed to CARs a single photon only results in a single chain scission event. Hence, the sensitivity of non-CARs will typically be less than CARs. However, recent advances in excimer laser technology will soon result in lasers with powers of 300W or greater, which is over six times that of lasers produced in 2005. With immersion scanner speeds at their current maximum, an excess of photons will be available to the lithographer, which opens up the possibility of the re-emergence of non-CARs. Due to the non-CAR solubility switch mechanism not being reliant on diffusion, significant improvements in LER are possible for non-CARs compared to CARs. For example, Gronheid *et al.* [4] has demonstrated that using poly(methyl methacrylate) (PMMA) as a non-CAR, they were able to pattern down to 21 nm using EUV photons, with much better LER than a commercially-available CAR. However, for non-CARs to be used in volume manufacturing the E_0 values to obtain such images needs to be significantly reduced.

Recently, we demonstrated that we were able to achieve a significant reduction (up to 7 times reduction) in E_0 by reducing the film thickness of PMMA resist films to ~ 20 nm [5]. This was attributed to an interaction of the polymer with the surface, which causes an increase in the free volume of the polymer. This postulation was supported by

Advances in Resist Materials and Processing Technology XXVI, edited by Clifford L. Henderson,
Proc. of SPIE Vol. 7273, 72733X · © 2009 SPIE · CCC code: 0277-786X/09/$18 · doi: 10.1117/12.814076

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

evidence from grazing angle-attenuated total reflectance-Fourier transform infrared spectroscopy (GATR-FTIR) for films of varying thicknesses.

In this paper we investigate the possibility of polysulfones being used as non-CARs for 193 nm immersion lithography. Polysulfones are a copolymer of sulfur dioxide and a vinyl monomer. Typically, this class of polymers exhibits sensitivities to ionizing radiation, which are up to six times greater than that of PMMA. Polysulfones also exhibit another interesting property, which is that they are thermodynamically unstable above a critical temperature, termed the ceiling temperature (T_c). Hence, once a radical forms on the polymer backbone as a result of a chain scission reaction, they have a tendency to spontaneously depolymerize when heated above T_c. This provides a possible mechanism for decreasing the molecular weight of the polymer in a post exposure (PEB) step, which is conducted outside of the exposure tool. Hence, the amount of SO_2 released in the tool can be minimized and the sensitivity of the resists can be increased.

2. EXPERIMENTAL

Sulfur dioxide (4 mL, 7.8 x10-2 mol) was condensed into a flask containing norbornene (500 mg, 5.3 x10-3 mol). The mixture was thoroughly degassed to remove residual oxygen and the solution was warmed to -20 °C. Dichloromethane (2 mL) was added followed by tert-butylhydroperoxide (t-BuOOH) (1 mol% based on norbornene, 6 M solution in decane) *via* a degassed syringe. The reaction was stirred at -20°C for four hours, before being warmed to room temperature to allow excess SO2 to evaporate. The residue was dissolved in DCM and the product precipitated into methanol. 1H NMR ($CDCl_3$): δ 3.8-4.1 (br m, backbone CH2CH2), 2.87 (br d, 2 x (α-CH at ring junction)), 2.05-2.15 (br m, bridgehead CH2), 1.5-1.7 (br m, 2 x (β-CH2 of six membered ring)).

PNS was dissolved in propylene glycol methyl ether acetate, with no PAG added. The solutions were then coated onto unprimed silicon wafers with an approximately 2 nm SiO2 native oxide layer. A post apply bake was performed at 120 ºC for 60 s. 193 nm irradiations were initially performed using a GAM EX10 excimer laser. Samples were also exposed at the Sematech facility in Albany. Irradiation doses typically ranged from 0-2000 $mJ.cm^{-2}$. For the post exposure bake studies, the temperatures used varied between 90-170 ºC. A developer was selected by testing the dark loss of various mixtures of isopropanol and cyclohexanone.

Film thicknesses and other optical properties were modelled based on optical parameters obtained from a Woollam VUV-VASE. FTIR spectra of thin films on Si wafers were obtained using a Thermo Nicolet FTIR spectrometer using a Harrick grazing angle attenuated total reflectance accessory fitted with MIR polarizers.

3. RESULTS AND DISCUSSION

Polynorbornene sulfone (PNS) was synthesized by the free radical polymerization of sulfur dioxide and norbornene, using *tert*-butyl hydroperoxide as an initiator. The structure of PNS is shown in Figure 1. PNS has a T_g of 121 °C, a refractive index of 1.74 at 193 nm and an absorbance of approximately 0.17 μm^{-1}. PNS has a reported G scission (G_s) value for ionizing radiation of 6.4 [6], which is high compared to PMMA, with a G_s value of 1.3. G_s is the number of chain scissions per 100 eV of absorbed radiation. This high G_s value and moderate T_g make PNS an interesting starting point for the design of non-CAR polysulfone based resists. This polymer has been previously evaluated as an e-beam resist [6].

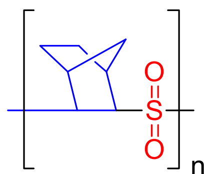

Figure 1 Structure of poly(norbornene-sulfone), (PNS).

3.1 Effect of irradiation

The chemical contrast curve for irradiation of PNS with 193 nm photons (Figure 2) exhibits a linear decrease in film thickness with dose, at a rate of approximately 5.1% $J^{-1}.cm^2$. This is consistent with random chain scission of the polymer backbone and loss of a small molecule. A linear loss of thickness with dose has also been observed for other

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

chain scissioning polymers, such as PMMA, where the loss of thickness for approximately 60 nm films was 12.8% $J^{-1}.cm^2$ [5]. It is difficult to directly compare these values, because the polymer structures and chain scission mechanisms differ, that is that PMMA is a homopolymer and PNS is an alternating copolymer of SO_2 and norbornene. This will be discussed further below.

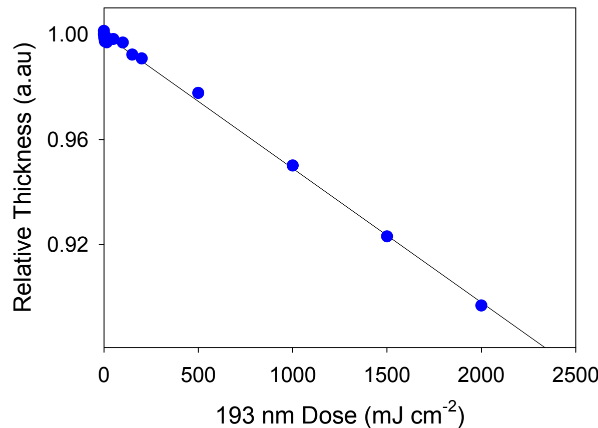

Figure 2 VUV-VASE chemical contrast curve for PNS

The GATR spectra of the films are shown in Figure 3 (a). GATR allows the FTIR spectra of very thin films on high refractive index substrates to be collected, which is not possible with conventional ATR.[7] The spectra exhibit a decrease in the sulfone bands at 1302 and 1143 cm^{-1} with increasing dose.[8] The decrease in sulfone bands is consistent with loss of SO_2 during irradiation, presumably through the scission of the C-S bonds, and is consistent with reports of the photo and radio-chemical degradation of aliphatic polysulfones. The decrease in the sulfone peak at 1302 cm^{-1} was found to be linear with 193 nm dose (Figure 3 (b)), with a rate of approximately 38% $J^{-1}.cm^2$. It is assumed that any norbornene monomer that forms during irradiation will remain on the wafer, because its boiling point is 96 °C. Hence, all the mass loss can be assumed to be due to evolution of SO_2 gas. The PNS used in these experiments has a degree of polymerization of 12800, hence if we assume that no depolymerization occurs then, there are approximately 4800 chain scissions per polymer chain $J^{-1}.cm^2$ or 4.8 scissions per polymer chain $mJ^{-1}.cm^2$.

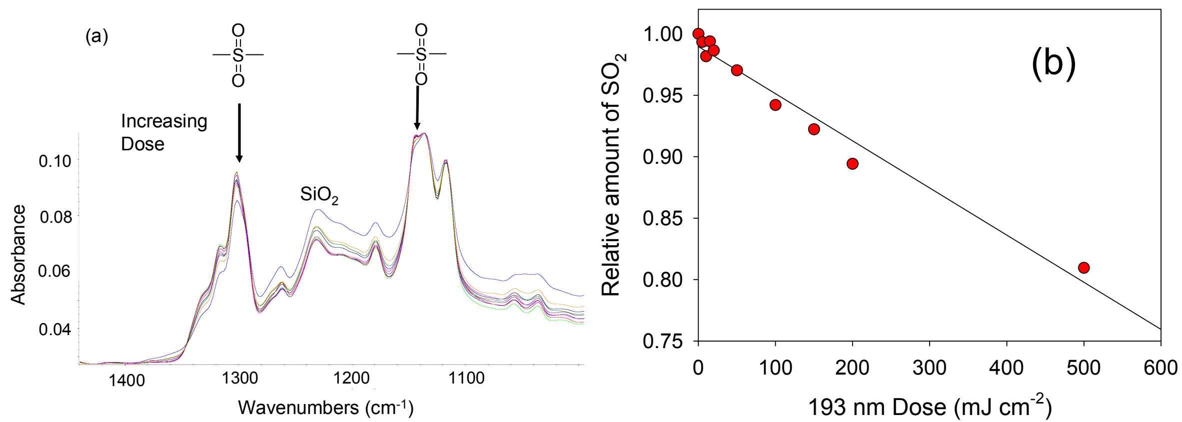

Figure 3 (a) GATR spectra of PNS irradiated with various doses of 193 nm photons, (b) Relative amount of sulfone repeat units remaining after irradiation

Development of the irradiated films using a non-optimized developer (100% isopropanol) resulted in further film loss compared to the irradiated-only films at a rate of 124%$J^{-1}.cm^2$. Again this loss was approximately linear with dose, up to the E_0, which is again consistent with random chain scission of the polymer backbone. This demonstrates that the thickness loss and evolution of SO_2 are associated with chain scission events along the PNS backbone.

Figure 4 shows the mechanism of photodegradation of PNS. The evidence presented above indicates that absorption of 193 nm photons by the polymer is resulting in random chain scission of the polymer backbone and

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

evolution of a small amount of sulfur dioxide. As a result of chain scission the molecular weight of the polymer is also decreasing. This is consistent with literature reports of the photo and radiochemical degradation of aliphatic polysulfones.

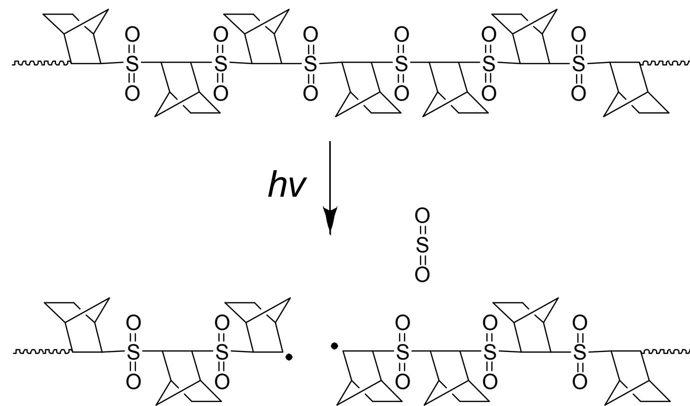

Figure 4 Mechanism of chain scission, involving scission of C-S bonds and loss of SO_2.

Effect of PEB

The temperature stability of un-irradiated PNS was established using thermogravimetric analysis (TGA). In Figure 5 the TGA curve for PNS is shown, where relative mass remaining is shown on the y-axis. The curve indicates that almost no mass loss is observed until approximately 200 °C, where a degradation onset is observed. Hence, this polymer should be able to withstand baking temperatures up to 200 °C.

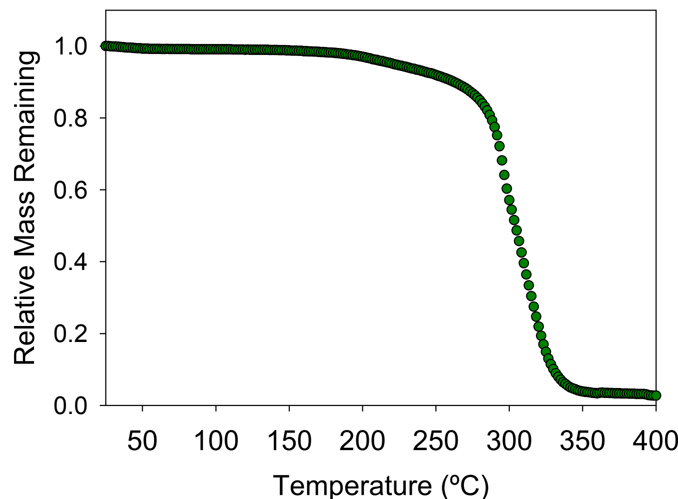

Figure 5 TGA curve for thermal degradation of unirradiated PNS

To determine if depolymerization of the polymer could be observed as a result of a PEB step the irradiated films were baked at a series of temperatures ranging from 90-170 °C. Spectroscopic ellipsometry showed that the thickness of irradiated films decreased for all bake temperatures (Figure 6), where generally the largest thickness losses were observed at higher bake temperatures, and the rate of thickness loss per dose was found to increase at higher bake temperatures. The Arrhenius plot in Figure 6 (b) is linear, which indicates that a single mechanism is dominating the depolymerization reaction. From this plot an activation energy of 88.7 kJ mol^{-1} can be calculated. These results suggest that depolymerization is occurring during the PEB step.

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

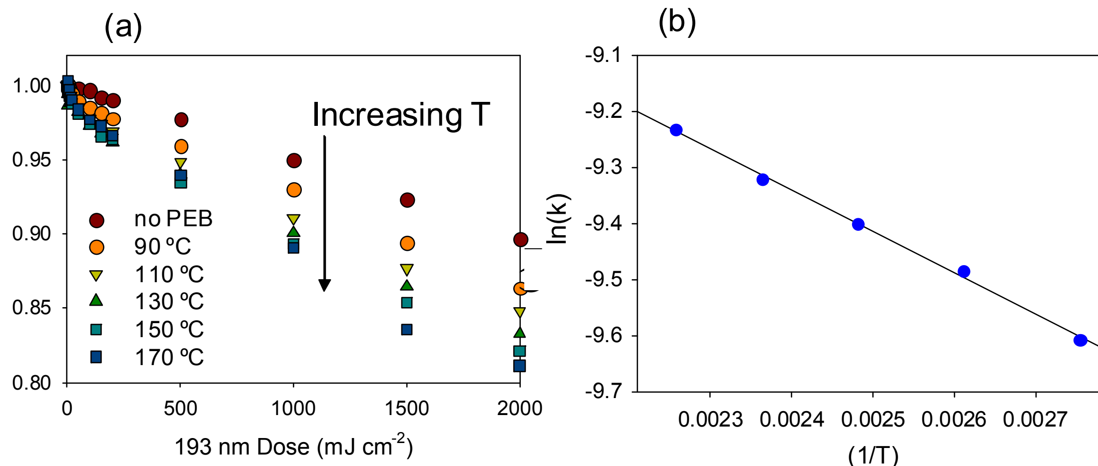

Figure 6 (a) Chemical contrast curves after PEB at various temperatures (b) Arrhenius plot for rate of film thickness loss per 193 nm dose and a variety of PEB temperatures.

Figure 7 shows the GATR spectra of PNS films irradiated to a dose of 500 mJ.cm^{-2} both before and after a PEB step. A decrease in the SO_2 band at 1302 cm^{-1} can be observed after the PEB step. Again this provides further evidence for depolymerization of the irradiated polymer.

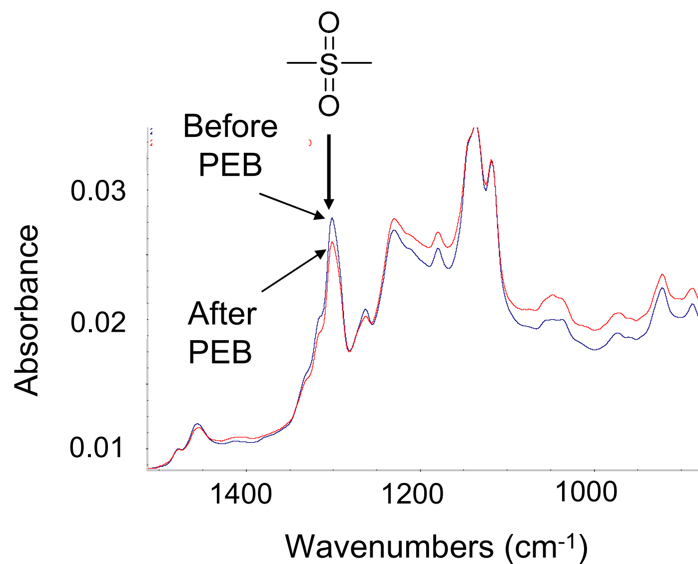

Figure 7 GATR spectra of PNS films irradiated to a total dose of 500 mJ cm^{-2} before and after PEB at 170 °C.

Figure 8 shows the contrast curve after irradiation and a PEB step at 170 °C. The developer used in this case was 60% isopropanol and 40% cyclohexanone, with a rinse time of 120s. A dramatic decrease in thickness with dose is observed, with an E_0 evident at approximately 50 mJ.cm^{-2} for this developer system. This demonstrates that the depolymerization that is occurring during the PEB is significantly decreasing the molecular weight of the polymer.

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

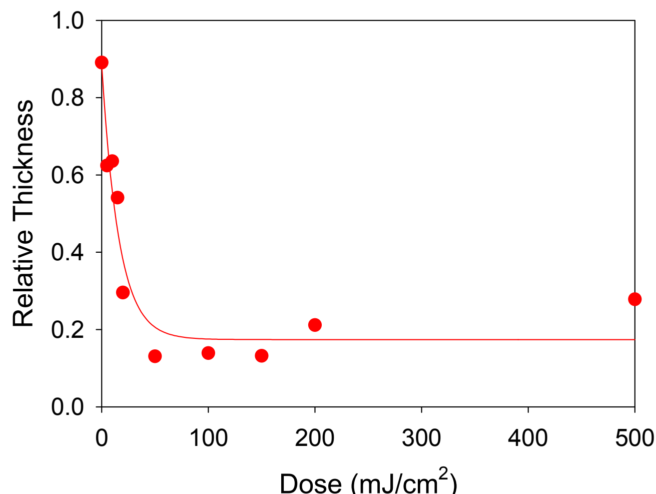

Figure 9 Contrast curve for PNS films, using 40% cyclohexanone and 60% IPA as a developer, after a PEB at 170 °C.

GATR of the films were also measured after solvent development. A general decrease in all the polymer peaks can be observed after development. At a dose of 100 mJ.cm^{-2} a small amount of residual polymer can be observed. However, the size of the peaks is very small compared to the peaks related to the 2 nm SiO_2 layer, which qualitatively suggests that this residue is very thin, i.e. much less than 1 nm thick. Degradation studies of aliphatic polysulfones with ionizing radiation have shown that side reactions can occur to a small degree.[9] This residual layer may be due to these side reactions and further optimization of the developer may be required to remove this residual layer. However, it also been demonstrated that certain side reactions can be suppressed by incorporation of cationic scavengers during degradation.[9] The relative height of the SO_2 band can be compared with the SiO_2 band. After development a similar curve to the contrast curve is obtained.

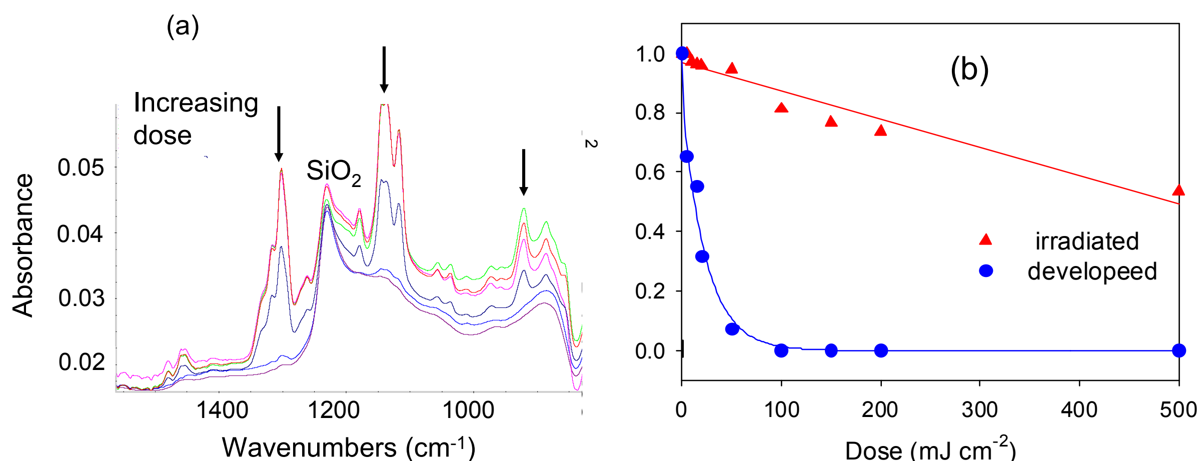

Figure 10 (a) GATR spectra after development at a variety of 193 nm doses. (b) Relative SO_2 concentration after irradiation (triangles) and development (squares)

Discussion of Mechanism

Ellipsometry and GATR data shows that depolymerization is occurring as a result of the PEB step. The developing step is consistent with molecular weight decreases during PEB, which is further support for depolymerization. These results are consistent with literature on depolymerization of aliphatic polysulfones. The depolymerization of irradiated polymer is occurring below the reported T_c of PNS, 157 °C, and there appears to be no discontinuity in the rate of degradation in temperature range used (90-170 °C). A likely reason for this is that the depolymerization is an equilibrium reaction and typically T_c values are determined in the presence of excess monomers. However, in our case the depolymerization occurs with no monomer present and on an open hotplate such that the generated SO_2 is dissipated. At higher

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

temperatures, >96 °C it is also likely that the norbornene monomer that is formed will readily volatilize. These factors will drive the equilibrium towards depolymerization and is likely to result in a depolymerization temperature that will be lower than the T_c [10]. Based on the Arrhenius plot in Figure 6 (b) the depolymerization temperature in the absence of monomer is less than 90°C. This is a positive result because the T_g of the polymer is 121 °C, and hence an effective bake temperature may be found below the T_g of the polymer, which will be important for the applicability of this class of polymers in lithography applications.

PNS is relatively transparent to 193 nm photons, with an absorbance of 0.17 μm^{-1}. The next step in the development of these polymers is to increase the absorbance of the polymer by inclusion of a small amount of a chromophore.

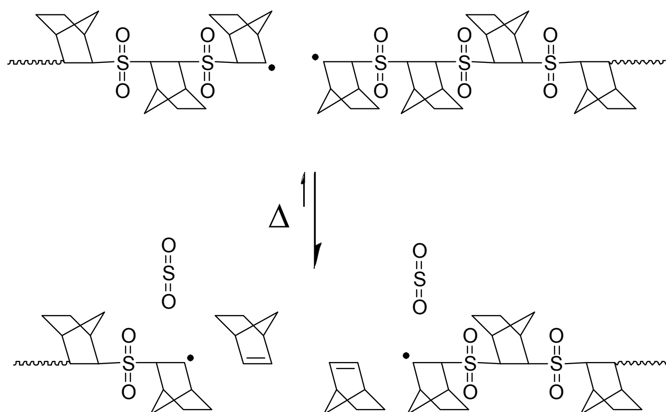

Figure 11 Radical depolymerization mechanism for PNS

SO_2 release

A concern with the use of these polymers is the release of SO_2 into the tool during irradiation. A worst case scenario is that 100% of the SO_2 is released during irradiation. For a 50 nm thick film of PNS this corresponds to 0.032 nmol of SO_2 released per $mJ.cm^{-2}$. However, this is somewhat of an over estimation. A more realistic scenario is based on the FTIR results, which indicate that at a dose of 100 $mJ.cm^{-2}$ to the wafer, approximately 5% of the SO_2 which corresponds to 0.0016 nmol of SO_2 released per $mJ.cm^{-2}$. SO_2 is extremely soluble in water at room temperature, so these small amounts of SO_2 will readily dissolve in the immersion fluid.

Patterning

At this stage no patterning results have been performed using 193 nm photons. However, a structurally similar polymer, poly(1-butene sulfone) has been patterned with EUV photons. An example of 50 nm HP results is shown in Figure 12. These results indicate that it is possible to pattern polysulfones. In this case a PEB step has not been used to reduce E_0 values. However, it is expected that a PEB step will further reduce the dose required.

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

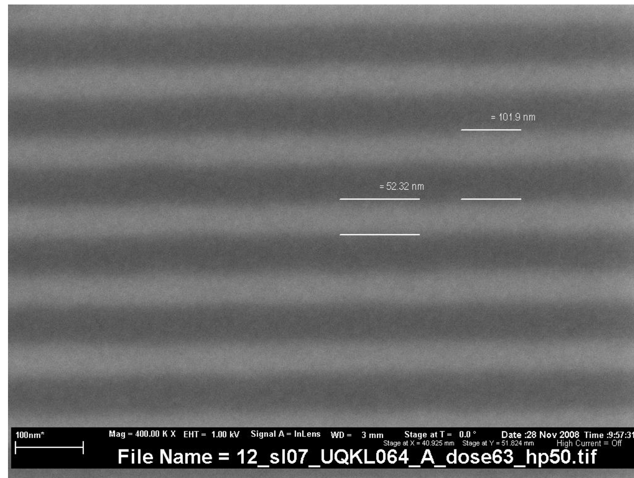

Figure 12 EUV patterning result for a poly(1-butene sulfone) film.

4. CONCLUSIONS

Irradiation of polysulfones with 193 nm photons results in film thinning and a decrease in SO_2 content. A PEB step was shown to result in depolymerization, which accentuated the molecular weight decrease and consequently increased contrast. After development with 60% IPA and 40% cyclohexanone, an E_0 of <50 mJ was obtained. Calculations show that the amount of SO_2 liberated during irradiation will be easily dissolved in immersion fluid.

5. ACKNOWLEDGEMENTS

This research was supported under the Australian Research Council's (ARCs) Linkage Projects Scheme (project number LP0882551), with Sematech as a financial industry partner. Equipment used in this research was supported by the ARCs Linkage Equipment, Infrastructure and Facilities funding schemes (project numbers LE0668517 and LE0775684). This work was performed in part at the Queensland node of the Australian National Fabrication Facility, a company established under the National Collaborative Research Infrastructure Strategy to provide nano and microfabrication facilities for Australia's researchers. This work was performed in part at the Bio-Nano Development Facility, which was funded by the Queensland State Government Smart State Innovation Building Fund. Some samples were irradiated at the Paul Scherer Intitut.

We acknowledge Dr. Lauren Butler for performing VUV-VASE measurements.

6. DISCLAIMER

SEMATECH and the SEMATECH logo are registered service marks of SEMATECH, Inc. All other service marks and trademarks are the property of their respective owners.

REFERENCES

[1] Jack, K., Liu, H., Blakey, I., Hill, D., Wang, Y., Cao, H., Leeson, M., Denbeaux, G., Waterman, J., and Whittaker, A., "The rational design of polymeric EUV resist materials by QSPR modelling," Proc. SPIE-Int. Soc. Opt. Eng., 6519(Pt. 2, Advances in Resist Materials and Processing Technology XXIV), 65193Z/1-65193Z/8 (2007).

[2] Bowden, M. J., and Thompson, L. F., "Poly(1-butene sulfone) as a positive electron resist," Appl. Polym. Symp., 23, 99-106 (1974).

[3] Bowden, M. J., Thompson, L. F., and Ballantyne, J. P., "Poly(butene-1 sulfone), a highly sensitive positive resist," J. Vac. Sci. Technol., 12(6), 1294-6 (1975).

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

[4] Gronheid, R., Solak, H. H., Ekinci, Y., Jouve, A., and Van Roey, F., “Characterization of extreme ultraviolet resists with interference lithography,” Microelectron. Eng., 83(4-9), 1103-1106 (2006).
[5] Blakey, I., Chen, L., Goh, Y.-K., Piscani, E., Zimmerman, P. A., and Whittaker, A. K., "Exploring Non-CA Resists for 193 nm Immersion Lithography," The International Symposium on Immersion Lithography Extensions, (2008).
[6] Gipstein, E., Moreau, W., Chiu, G., and Need, O. U., III, “The synthesis and evaluation of cyclic olefin sulfone copolymers and terpolymers as electron beam resists,” J. Appl. Polym. Sci., 21(3), 677-88 (1977).
[7] Mulcahy, M. E., Berets, S. L., Milosevic, M., and Michl, J., “Enhanced Sensitivity in Single-Reflection Spectroscopy of Organic Monolayers on Metal Substrates (Pseudo-ATR),” The Journal of Physical Chemistry B, 108(5), 1519-1521 (2004).
[8] Lin-Vien, D., Colthup, N. B., Fateley, W. G., and Grasselli, J. G., [The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules] Academic Press, San Diego(1991).
[9] Bowmer, T. N., O'Donnell, J. H., and Wells, P. R., “Radiation degradation of poly(sulfonylalkylene)s: evidence for cationic reactions,” Makromol. Chem., Rapid Commun., 1(1), 1-6 (1980).
[10] Bowmer, T. N., and O'Donnell, J. H., “Thermal degradation of poly(olefin sulfone)s. Part I. The effect of olefin structure on the yields of volatile products,” Polym. Degradation Stab., 3(2), 87-95 (1981).

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/04/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx