

The Rational Design of Polymeric, EUV Resist Materials by QSPR Modelling

Kevin Jack^{*+}, Heping Liu^{*+}, Idriss Blakey^{*+}, David Hill^{*^}, Wang Yueh[†], Heidi Cao[†], Michael Leeson[†], Greg Denbeaux[‡], Justin Waterman[‡] and Andrew Whittaker^{*+}.

^{*}Centre for Magnetic Resonance, ⁺Australian Institute for Bioengineering and Nanotechnology and the [^]School for Molecular and Microbial Science, The University of Queensland, St Lucia, Queensland 4072, Australia.

[†]Intel Corporation, Hillsboro, Oregon, USA.

[‡]College of Nanoscale Science and Engineering, University at Albany, Albany, NY 12203, USA.

ABSTRACT

We present the initial results of the development of a qualitative structure property relationship (QSPR) model to guide in the design and synthesis of high-sensitivity, non-CAR materials for EUV lithography. The model was developed using the fragmentation data of low molecular weight species at 70 eV using a mass spectrometer (MS) with an electron ionization source as the input parameter. The preliminary model has highlighted a number of structural elements which will be important in the future design of resists, however, limitations with the current set of input data for molecules which fragment readily have been identified and these are currently being addressed. Additionally, a correlation between γ (1 MeV) and EUV (92 eV) radiolysis of selected polymers has been established and it is proposed that the higher energy (1 MeV) irradiation source is a suitable model process for EUV and can, therefore, be used in the future screening of polymeric materials.

Keywords: EUV, Lithography, Non-CAR, Polymer, Resist, Polymer Degradation

1. INTRODUCTION

Extreme ultra-violet (EUV) lithography, in which the irradiation is carried out with 13.4 nm (~ 92 eV) photons, is one of the candidates for next generation lithography, with the potential to permit the patterning of features 32 nm^{1,2} and below. Although a number of limitations in currently available technologies need to be addressed, *e.g.* the design of better optical devices and higher intensity 13.4 nm photon sources, the development of resist materials for EUV lithography is currently one of the major challenges. Specifically, these challenges include the development of materials that have: a low absorption cross section (*i.e.* high transmittance), high sensitivity and contrast to 13.4 nm radiation, minimal production of volatile components (*i.e.* low out gassing) and low line-edge roughness (LER) values. Indeed, it is the achievement of the last criterion that is believed to be the most difficult, with target values of $3\sigma \leq 1.5$ nm being sought for the 45 and 32 nm nodes³.

Current research efforts include investigations of polymeric systems containing photoacid generators (PAG) (see *e.g.*⁴), molecular glasses (with or without PAG) (see *e.g.*⁵) and multilayer resists (see *e.g.*²). To date, however, there are no resist formulations which are capable of meeting all of the requirements above or, indeed, even the target LER values. Additionally, current resist technology relies heavily on the use of photo-acid generators (PAG) to chemically amplify the response of the resist formulation to the incident radiation. However, depending on the resist formulation and lithography conditions used the diffusive path-length of the PAG may be as high as 50 nm, a significant size compared with the feature size (sub-50 nm) and target LER criteria of emerging lithography technologies. Even with optimization of the resist formulations and conditions the diffusive path-length can only be limited to tens of nm. A need, therefore, exists to investigate and develop non-chemically-amplified resists (non-CAR) with high sensitivities, comparable to those of the PAG-based systems.

The details of quantitative structure property relationship (QSPR) modeling have been reported previously.^{6,7} Recently, we have demonstrated how the generation of a QSPR model can be used to guide in the development of high refractive index (RI) resist materials for 193 nm immersion lithography⁸. The model was generated from RI measurements, at 589 nm, of 126 small organic compounds and a basis set of 791 descriptors. It was found that nine descriptors (which can be related to structural elements in the compounds) were significant in determining the RI of the materials. This in turn has been used to guide the synthesis of a number of polymers with RI > 1.8, in agreement with the prediction of the model.

In this paper we present the initial results of the development of a QSPR model to predict the rate of degradation of polymeric materials as a function of the chemical constituents in both the main and side chains of the polymer structure. The QSPR model was developed using data obtained from the fragmentation of low molecular weight species at 70 eV using a mass spectrometer (MS) with an electron ionization source. 70 eV fragmentation was chosen as a means to enable high-throughput determination of the fragmentation of a library of compounds that covers a significantly diverse region of chemical space so that a robust QSPR model can be generated. The method also has the advantage that it can screen species with volatile degradation products. In addition, correlations between γ (1 MeV) and EUV (92 eV) radiolysis of selected polymers are presented to verify that the higher energy irradiation source is a suitable model process for EUV and can, therefore, be used in the future screening of polymeric materials.

2. MATERIALS AND METHODS

Materials

Poly(methyl methacrylate) (PMMA) and poly(isobutylene) (PIB) were purchased from Aldrich Chemical Co. Poly(α -methyl styrene) (PAMS) was purchased from Polysciences. The PAMS and PMMA were used as received, while the PIB was precipitated to remove the added stabilizer. The small organic molecules were predominantly purchased from Aldrich and were used as received.

γ Irradiation

Irradiations were carried out in a *Nordion* Gammacell 220 which contains ⁶⁰Co fuel elements. ⁶⁰Co decays, with a half life of 5.27 years, to produce two γ photons with energies of 1.17 and 1.33 MeV. The adsorbed dose was measured by Fricke dosimetry⁹ and determined to be ca. 2.5 kGy h⁻¹ at the time of this work. The polymers were irradiated in glass ampoules sealed at a pressure of 10⁻³ mbar and at ambient temperature.

EUV Irradiation

Samples for EUV irradiation were spin-coated onto 150 mm diameter (100) silicon wafers on a ChemMat technologies spin coater. The PMMA and PAMS were dissolved in propylene glycol methyl ester acetate (PGMEA) and PiB was dissolved in cyclohexane. The appropriate concentrations and spinning rates were determined empirically by measuring the film thickness as a function of both parameters; typically a concentration of ca. 1.5 – 2.5% by weight and spinning rates on the order of 1.5 – 2.5 kHz were employed to achieve a film thickness of 50 nm. The thickness of the coated films were determined from ellipsometry (Gaertner L117 Null Ellipsometer) at an angle of 70° and further verified by AFM measurements.

Irradiation with EUV photons was carried out at the College for Nanoscale Science and Engineering, University at Albany, NY. The system used an *Energetic EQ-10M* xenon plasma source through a Zr filter to produce 10 – 15 nm radiation, which was operated at 10 W total power, with near 1 mw/cm² on the sample. The wafers were cleaved into ca. 12.5 mm x 150 mm rectangular sections and introduced into the irradiation chamber (10⁻⁶ mbar) via a load lock system. The appropriate dose was delivered to the entire wafer section by passing it through the EUV beam at a controlled rate. The incident beam intensity was measured using a photodiode. For each dose, eight wafer sections were irradiated to produce enough material (0.4 mg) for GPC analysis.

Gel Permeation Chromatography (GPC)

GPC measurements were performed using a Waters 2695 separation module with three linear (2 x Styragel followed by 1 x Ultrastaygel) columns in series. Samples (1 mg ml⁻¹ in THF) were eluted with THF at a rate of 1 ml min⁻¹ at 30 °C and detected using a Waters 410 differential refractometer. The molecular weight as a function of retention volume was calibrated using low polydispersity (PDI ~ 1.03) polystyrene standards and the molecular weights are reported with respect to polystyrene.

Gas chromatography and mass spectrometry (GC-MS)

GC-MS measurements were performed using a Shimadzu GCMS-QP5050 gas chromatography mass spectrometer with helium as the carrier gas. Temperature ramping from 50 to 250 °C at a rate of 10 °C min⁻¹ was used and the injector temperature was set to 250 °C. Electron ionization mode was used for the MS and the scan range was from 30 to 300 amu.

QSPR Models

The geometries of the model compounds were first optimized with the semi-empirical AM1 method¹⁰, using the AMPAC software package and then descriptors were calculated using the CODESSA¹¹ software package. The heuristic method was applied to find the best one-parameter correlations. Using these one parameter correlations the most significant descriptors were determined using multi-linear regression to find the best predictive model.

3. RESULTS AND DISCUSSION

3.1 Correlation of sensitivity at 1 MeV and 92 eV

As noted above, our initial aim is to determine if 1 MeV (γ) photons can be used as a predictor of the sensitivity and performance of polymeric resist materials at 92 eV. The results of radiolysis experiments carried out on poly(methyl methacrylate) PMMA and poly(isobutylene) PIB at both 1 MeV and 92 eV are presented in Figure 1. In this figure the inverse of the number-average molecular weight (M_n^{-1}), as measured by GPC, is plotted as a function of the irradiated dose (D). For polymers undergoing predominantly chain scission it can be shown that¹²:

$$M_n^{-1}(D) = M_n^{-1}(0) + 2 \cdot k_1 \cdot G(s) \cdot D \quad (1)$$

where $M_n^{-1}(0)$ is the initial M_n of the unirradiated polymer, k_1 is a constant and $G(s)$ is the yield of chain scission; the number of scission events per 16×10^{-18} J of energy absorbed. If D is expressed in kGy then $k_1 = 5.18 \times 10^{-8}$ (n.b. 1 Gray (Gy) is equal to an *absorbed* dose of 1 J per kg of material).

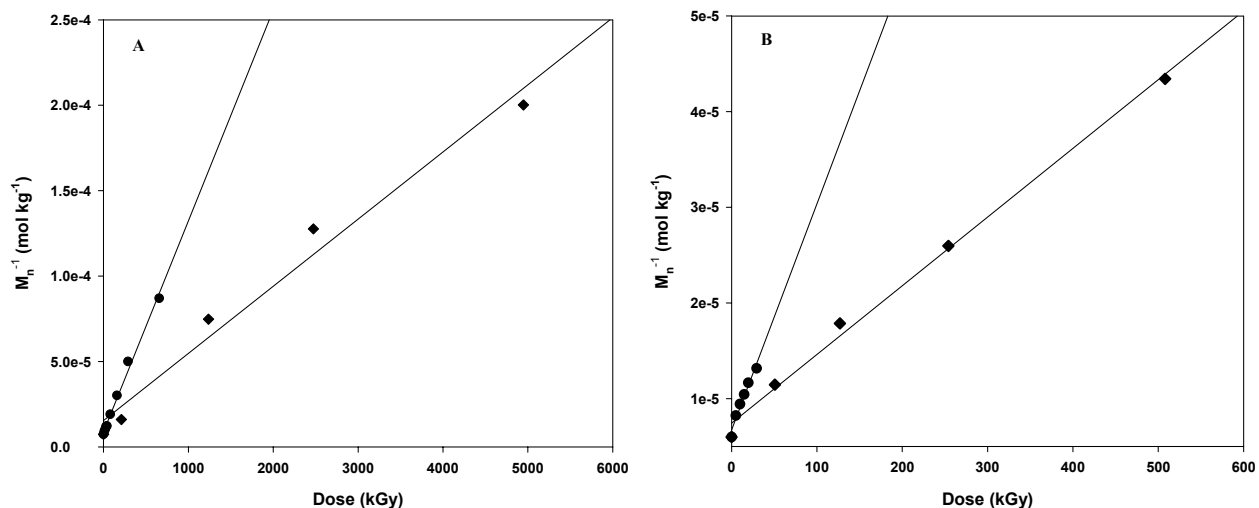


Figure 1. The radiolysis of A). PMMA and B). PIB at 1 MeV (circles) and 92 eV (diamonds). The solid lines are linear regressions (see Equation 1).

For all of the systems investigated, and at both 1 MeV and 92 eV, a linear increase in M_n^{-1} (*i.e.* a decrease in M_n) was observed with increasing dose (see *e.g.* Figure 1). From Equation 1 it is, therefore, possible to determine the yield of chain scission events $G(s)$ for the polymers at both energies. As noted above, the dose in the 1 MeV experiments was determined by Fricke dosimetry. However, in the case of the 92 eV radiolysis experiments it was not possible to carry out such dosimetry. The absorbed dose was, therefore, estimated by assuming that all of the energy of the absorbed photons (*i.e.* that which is not transmitted) is converted to kinetic energy of electrons, *i.e.* assuming $\mu_{en}/\rho \sim \mu/\rho$ (where μ_{en}/ρ is the unknown mass energy adsorption coefficient and μ/ρ is the known mass absorption coefficient). This assumption may lead to an overestimate of the true absorbed dose for the EUV radiolysis experiments, because it does not account for the possible loss of energy in the form of heat or fluorescence. The dose (D) in the case of the EUV experiments was, therefore, calculated as:

$$D = \frac{[1 - T(t)] \cdot I_0}{\rho \cdot t} \quad (2)$$

where $T(t)$ is the transmission of the polymer film of thickness t at 92 eV (obtained from¹³), I_0 is the initial, measured, photon intensity and ρ is the density of the polymer film.

In Figure 2, the $G(s)$ values determined from the EUV irradiations (given the caveat above in the case of EUV) are plotted as a function of the $G(s)$ values determined from the γ radiolysis experiments. For the three polymers investigated, here, there is a good correlation between the radiolysis yields for the two techniques. At this stage it is not clear if the lower $G(s)$ values determined for the EUV irradiations are a consequence of differing sensitivities at the different incident photon energies, or if they are due to an overestimate in the absorbed dose in the case of EUV and this needs further investigation. Nonetheless, the relative sensitivities of the polymers remain the same for both types of irradiation. These results demonstrate that the sensitivity of polymers at 1 MeV can, therefore, be used as a predictor of sensitivity at 92 eV. Moreover, the extensive body of literature and knowledge in polymer interactions with high energy ionizing radiation that exists already can be used to guide design rules for polymeric EUV resists. Finally, these results show that it is possible to use γ radiolysis as a preliminary screening technique for polymeric EUV resist formulations. The advantages of this include the current broader availability of γ sources and their relative insensitivity to contamination by gaseous products, compared with EUV sources.

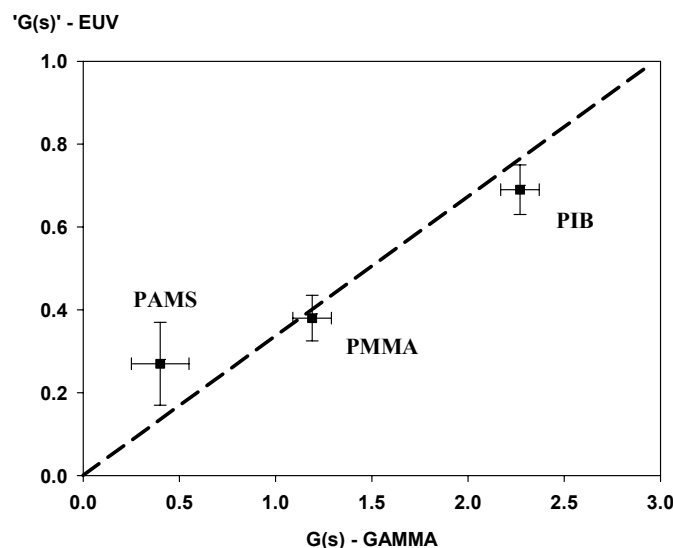


Figure 2. Correlation between $G(s)$ determined from γ and EUV radiolysis. $G(s)$ for the EUV is approximate as noted in the text above.

3.2 QSPR modelling of the sensitivity of polymer resist at 92 eV

Initial attempts to generate a QSPR model based on the values of $G(s)$ published in the literature for a range of polymers proved unfruitful, with correlation coefficients of less than 0.5 being achieved. This lack of success is most likely a result of the large range of conditions (*e.g.* temperature, pressure, irradiation sources and method of determination) used in these experiments; some of which were not fully detailed in the relevant literature. Therefore, it is necessary to measure experimentally a large body of input data under controlled conditions to generate a quantitative model. However, generating a comprehensive enough range of $G(s)$ values in a short period of time was considered to be too time consuming to be able to rapidly achieve the aims of this project, and an alternative set of model data is considered in this work. This data was collated by measuring the degradation of small organic molecules under electron impact in a standard mass spectrometer (MS) with an electron ionization source operating at 70 eV.

To quantify the degree of fragmentation of the molecules we define the relative molecular ion (RMI) ratio of each sample as the ratio of the ion count for the molecular ion to that of the total ion count measured. The lower the value of the RMI, the more extensive the fragmentation in the molecule being investigated, *i.e.* it is more sensitive to degradation by 70 eV electrons. In Figure 3 we show the mass spectrum of two representative small molecules along with their RMI values. In total we have, thus far, collected MS data for 76 small molecules. The RMI values for a range of these are presented in Figure 4.

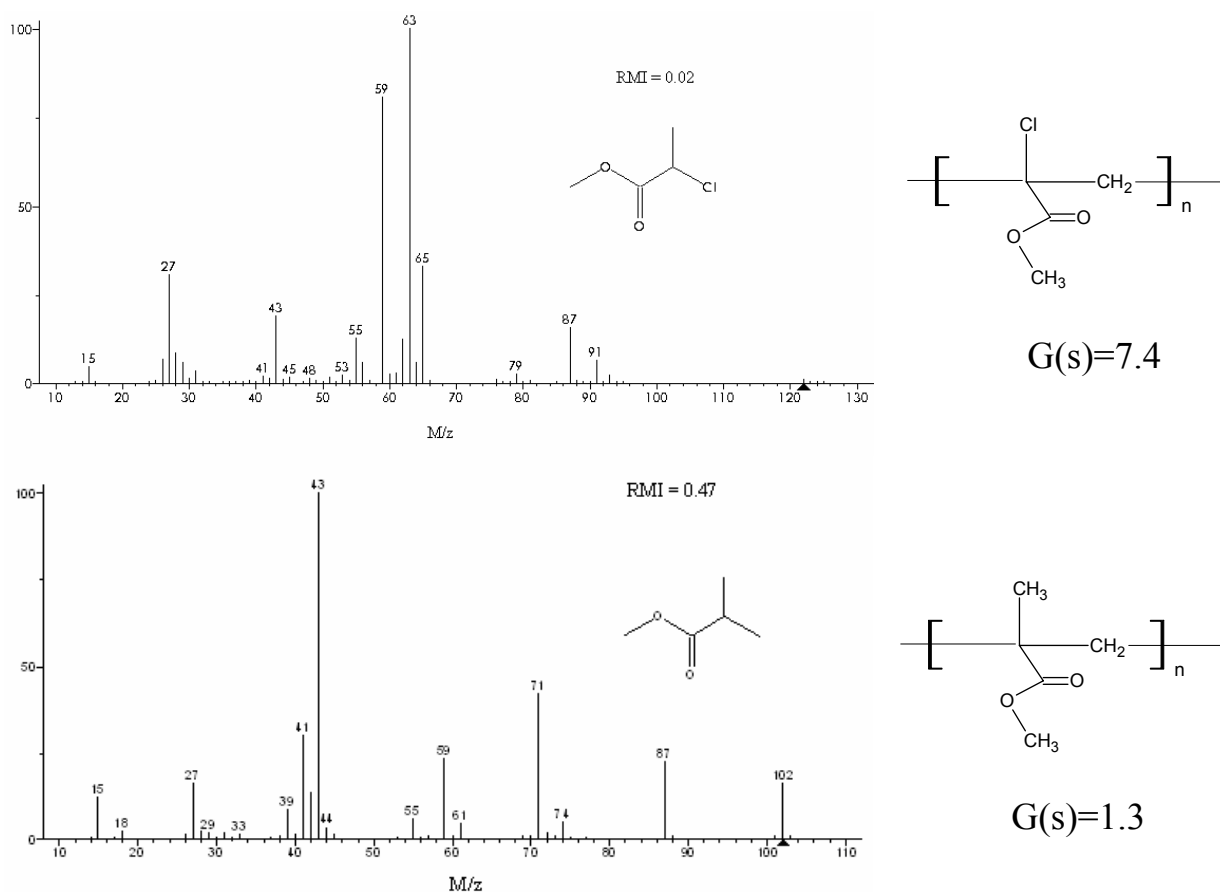


Figure 3. The 70 eV mass spectrum collected for A). Methyl 2-chloropropionate and B). Methyl isobutyrate, and the RMI values (see text) measured for each. Also shown are the polymer of the molecules and their $G(s)$ values at 1 MeV analogs [A). poly(chloro methacrylate) and B). poly(methyl methacrylate)].

3.2.1 Qualitative observations

Initially, we point out that there is a qualitative relationship between the value of the RMI and the sensitivity of analogous polymer structures to 1 MeV irradiation, and, hence, 92 eV irradiation (see Section 3.1 above). For example in Figure 3 we have also shown the 1 MeV G(s) values for the polymer analogs of the small molecules shown. It can be seen that the methyl 2-chloropropionate has both a significantly lower RMI (*i.e.* a higher degree of fragmentation) than the methyl isobutyrate and a correspondingly larger yield of chain scission in the analogous polymer. This qualitative observation lends support to the choice of the 70 eV data used in the development of the QSPR model below.

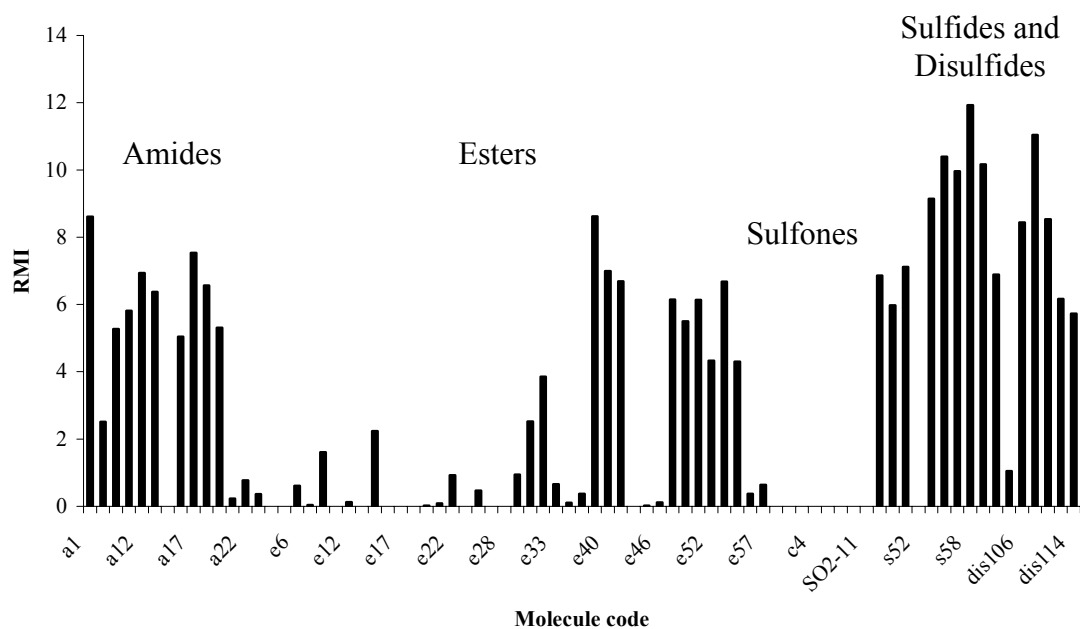


Figure 4. The RMI values measured for a range of small molecules; clustered by chemical functionality.

From the RMI values presented in Figure 4 it is further possible to group the data into sets with high and low RMI values and thereby gain insight into the functional groups that increase the sensitivity of the analogous polymers. In general, the analysis suggests that functional groups such as sulfones, halogens, carbonates, as well as electron-withdrawing groups and chain branching will lead to favorable increases in sensitivity. The sulfides, disulfides, aromatic and cyclic structures, however, were found to reduce sensitivity and hence should be avoided.

3.2.2 Development of a QSPR model

The initial attempt to produce a QSPR model based on the RMI values measured is shown in Figure 5. This figure shows the best correlation ($R^2 = 0.82$) that could be achieved from the RMI data collected to date. The model shown contains five descriptors which are related to:

- the energy of the highest occupied molecular orbital (HOMO)
- the partial charge on the molecule (three separate descriptors)
- the C-H bond strength.

Although the R^2 value for this model is too low for it to be considered a quantitative model, at present, the qualitative information contained within does provide some useful information in the general design rules for the resist (as discussed above).

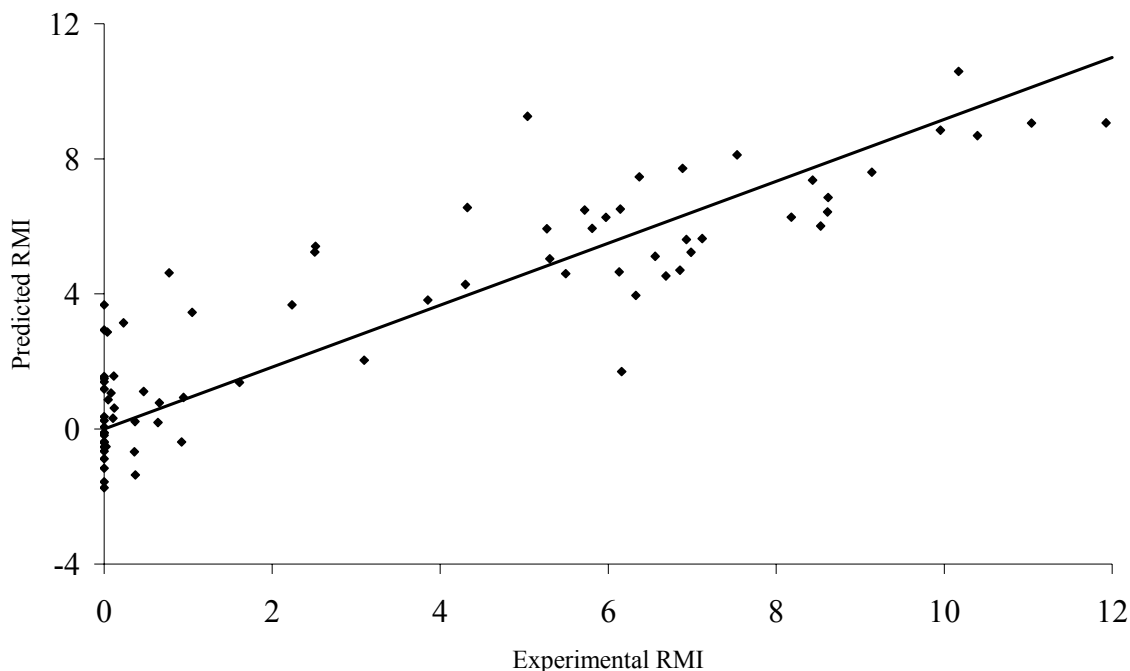


Figure 5. The initial QSPR model derived from the measurement of RMI values of small molecules; $R^2 = 0.82$

One significant limitation in developing a QSPR model based on the RMI data collected to date is the poor dispersion of RMI values for the highly fragmenting species with measured RMIs close to zero; *i.e.* those related to the materials with the highest sensitivities to degradation. It is necessary, therefore, to find a more sensitive method (*e.g.* using a lower flux of 70 eV electrons) which could allow for the separation of RMI values of the more highly fragmenting molecules. We are currently investigating methods for achieving a more quantitative and reliable model.

4. CONCLUSIONS

We have demonstrated a satisfactory correlation between the yield of scission products $G(s)$ at 1 MeV (γ) and 92 eV (EUV) for three pure polymeric materials. It should, therefore, be possible to use the knowledge and literature base on the effects of γ radiation on such polymers to guide in the design of polymeric resist materials with a high sensitivity to EUV. Additionally, it will also be appropriate to use 1 MeV radiolysis as a preliminary screening method for newly developed polymeric resists, with the advantage that it is possible to test a broader range of materials (*e.g.* materials whose out gassing properties are unknown). Preliminary investigations into the development of a QSPR model to guide in the synthesis of new resist materials with high 92 eV sensitivities were shown. The model uses input data from 70 eV electron ionization MS measurements of a large range of small molecules. Although, a satisfactory QSPR model is yet to be developed, the initial findings have highlighted a number of structural elements which will be important in the future design of resists.

5. REFERENCES

1. Levinson, H. J., *Principles of Lithography*, 2nd Edition, SPIE Press, Bellingham WA (2005).
2. Bratton, D., Yang, D., Junyan, D., Ober, C. K., "Recent Progress in High Resolution Lithography", *Polym. Adv. Technol.*, (2006), **17**, 94
3. Cao, H. B., Roberts, J. M., Dalin J., Chandhok M., Meagley R. P., Panning E. M., Shell M. K., Rice, B. J., "Intel's EUV Resist Development", *Proc. SPIE – Int. Soc. Opt. Eng.* (2003), **5039**, 484.
4. Watanabe, T., Hada, H., Lee, S. Y., Kinoshita, H., Hamamoto, K., Komano, H., "Development of Fast-Photospeed Chemically Amplified Resist in Extreme Ultraviolet Lithography", *Jap. J. Appl. Phys.* (2005), **44**, 5866.
5. Chang S. W., Ayothi R., Bratton, D., Yang, D. Felix, N., Cao, H. B., Deng, H., Ober, C. K., "Sub-50 nm Feature Sizes Using Positive Tone Molecular Glass Resists for EUV Lithography", *J. Mat. Chem.*, (2006), **16**, 1470.
6. Katritzky, A. R., Sild, S., Karelson, M. J., *Chem. Inf. Comput. Sci.*, (1998), **38**, 840.
7. Katritzky, A. R., Sild, S., Karelson, M. J., *Chem. Inf. Comput. Sci.*, (1998), **38**, 1171.
8. Whittaker, A. K., Blakey, I., Liu, H., Hill, D. J. T., George, G. A., Conley, W., Zimmerman, P., *Proc. SPIE-Int. Soc. Opt. Eng.* (2005), **5753**, 827.
9. O'Donnell J. H. and Sangster D. F., *Principles of Radiation Chemistry*, Edward Arnold Pub. LTD, London (1970)
10. Dewar, M. J. S., Zoebisch, E. G., Healy, E. F., Stewart, J. J. P., "Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model", *J. Am. Chem. Soc.* (1985), **107**, 3902.
11. Katritzky, A. R., Lobanov, V. S., Karelson, M., "CODESSA, Reference Manual", Semichem and the University of Florida, (1997).
12. Charlesby, A., *Proc. Roy. Soc. (London)* (1954), **A224**, 120.
13. A) Henke B.L., Gullikson E.M., and Davis J.C., "X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92", *Atomic Data and Nuclear Data Tables* (1993), **54 (no.2)**, 181-342. B). http://www.cxro.lbl.gov/optical_constants/