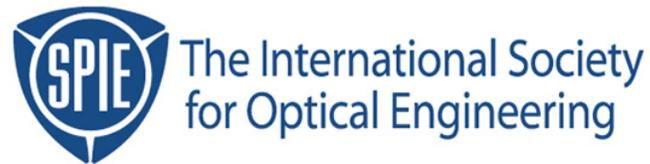


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# Diffusivity Measurements in Polymers, Part IV: Acid Diffusion in Chemically Amplified Resists

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## Abstract

Many of the strategies for sub 0.25  $\mu\text{m}$  lithography depend on chemically amplified resists to provide sensitivity. For example, glass damage limits the dose that can be delivered at 193 nm, and source brightness limits the dose that can be delivered in the EUV. However, acid diffusion, an integral part of the chemical amplification process, dramatically affects the lithographic performance of chemically amplified resists [1]. The transport properties of Brønsted acids in glassy polymers have been estimated from a variety of indirect measurements [1]. We have, for the first time, *directly* measured the diffusion coefficients of acids in polymer films.

A Quartz Crystal Microbalance (QCM) was used to make the measurements. The QCM can detect small changes in mass which is indicated by a shift in the resonant frequency of the piezoelectric quartz crystal (see the accompanying paper "Diffusivity Measurements in Polymers, Part III: Quartz Crystal Microbalance Techniques"). The experiments were conducted at different temperatures in order to establish the dependence of the diffusion coefficient on temperature. Acid diffusion in poly(hydroxystyrene) will be discussed.

**Keywords:** acid diffusion, quartz crystal microbalance, chemically amplified resist, Fickian diffusion

## 1. Introduction

The ultimate resolution of a refractive lens based printing technique is governed by the wavelength of light used in exposure, and therefore the semiconductor industry is moving towards smaller wavelengths to achieve better resolution. However, deep-UV ( $< 250$  nm) exposure tools with mercury lamp illuminators have low intensity at these wavelengths. In addition, absorption by conventional photoresists is high in the deep-UV region. Therefore, resists with greater sensitivity and very efficient processes are needed. The quantum yield for conversion of insoluble material to soluble material in conventional resists is much less than 1.0, which is not adequate for the low intensity illumination sources [2]. The only way to achieve the required improvement in sensitivity is with chemical amplification.

Systems with chemical amplification (CA) are those in which an initial photochemical event produces a catalyst. This catalyst then acts on the surrounding matrix and can lead to a cascade of subsequent reactions that affect a change in the solubility of the parent material. In general, CA resists use a photochemically generated acid to catalyze crosslinking or deprotection

reactions. The sensitivity of resists that are based on chemical amplification can be as much as several orders of magnitude greater than that of resists which consume at least one photon for every functional conversion [2].

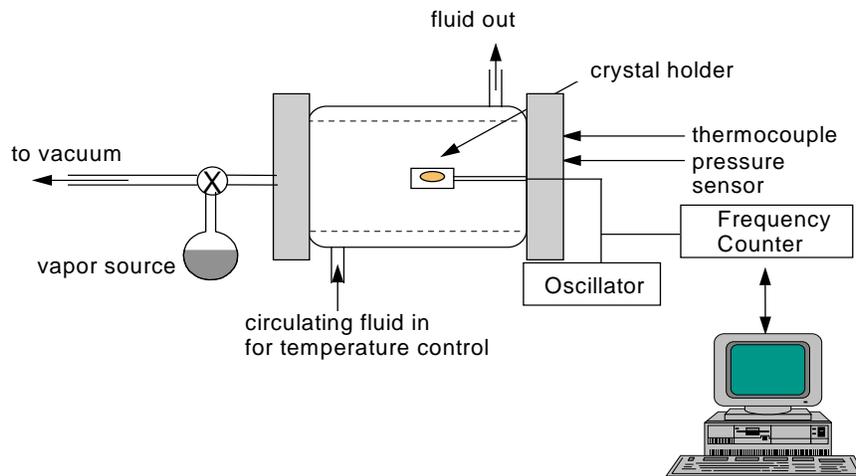
A typical chemically amplified resist consists of a matrix polymer, photoacid generator (PAG), and a group that is capable of effecting the differential solubility between the exposed and unexposed regions of the film.

Acid diffusion can dramatically affect the lithographic performance of chemically amplified resists [1]. On one hand, acid diffusion is needed to reduce the effects of standing waves, on the other hand, however, too much acid diffusion blurs the latent image. Therefore, knowledge of the diffusion coefficient of the acidic species is needed in order to predict the amount of diffusion that will occur for a given bake condition, and post exposure delay. Many have attempted to measure acid diffusion indirectly [3-5] but no direct measurement of acid transport has been reported.

In this study a Quartz Crystal Microbalance (QCM) was employed to produce mass versus time data. By using this technique, we were able to directly measure acid diffusion in poly(hydroxystyrene). The following sections contain the experimental details, along with the results and conclusions.

## **2. Experimental**

The experiments were performed by means of a quartz crystal microbalance that is shown in Figure 1 (see the accompanying paper "Diffusivity Measurements in Polymers, Part III: Quartz Crystal Microbalance Techniques"). 6 MHz Quartz crystals with polished gold electrodes were coated with a poly(hydroxystyrene) film ( $M_n = 32,000$ ,  $M_w = 70,000$ ) by spin coating at 2500 RPM for 30 seconds. Polished quartz crystals were obtained from Phelps Electronics and the deposition system was purchased from Leybold Inficon. The poly(hydroxystyrene) was dissolved in propyleneglycol methyl ether acetate (PGMEA) to 20 wt.%. The acids that were investigated included trifluoroacetic acid and methanesulfonic acid (triflic acid).



**Figure 1.** Quartz Crystal Microbalance

The thickness of the films was measured by using a multi-wavelength reflectance measurement technique. After coating, the films were hotplate baked at 90 °C for 90 seconds. The crystals were then inserted into the crystal holder and vacuum was applied until there was no change in the frequency, indicating a dry film. The entire system was maintained at a constant temperature by circulating a water/ethylene glycol mixture through the double-walled sample chamber and the crystal holder. That portion of the apparatus that was not heated by the circulating fluid was maintained at a constant temperature through the use of heating tape and insulation. The temperature was monitored by surface adhesive J-type thermocouples.

Acid, which is maintained at a constant temperature by another heating bath, was then introduced into the chamber, and mass uptake was observed by monitoring the change in frequency. The data were written to a spreadsheet through the use of a Labview<sup>®</sup> program which records the frequency and time for each data point. Once a sorption run was complete, the solvent supply was closed, the system evacuated and a desorption run was carried out. Thus, the measured output for both sorption and desorption experiments was the mass of the film as a function of time, giving a direct measurement of the amount of acid diffusing into and out of the film.

### 3. Results and Discussion

The data of mass versus time can be analyzed to determine the diffusion properties of the acid in the polymer film. Beginning with the simple assumption that the acid diffusion coefficient is not concentration dependent, the diffusion coefficient may be evaluated using conventional Fickian equations for one-dimensional diffusion in a plane sheet. In order to use this form of the equation, the film must be sufficiently thin such that all of the diffusing media enters through the plane face of the film [6]. The solution to Fick's law using the appropriate boundary conditions is given by the following expression:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right\} \quad (1)$$

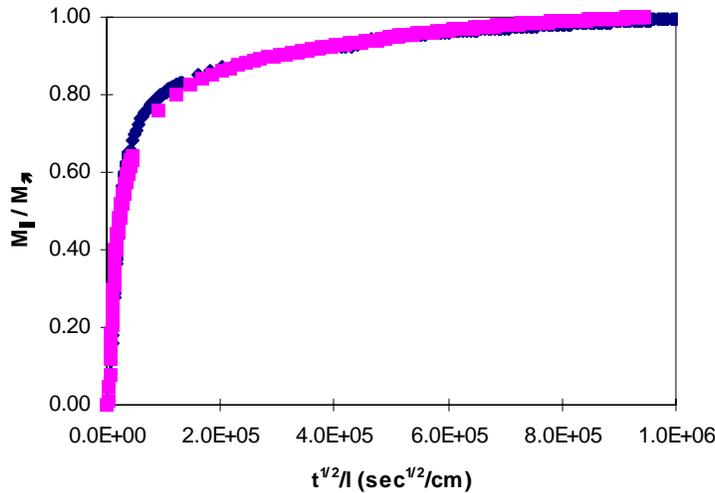
where  $M_t/M_\infty$  is the percentage of mass uptake,  $t$  is the time,  $l$  is the thickness of the film, and  $D$  is the diffusion coefficient.

Another expression that is useful for small times is given by equation 2. By plotting  $M_t/M_\infty$  versus  $\sqrt{t}/l$ , the short-time diffusion coefficient may be determined from this expression.

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{l^2}\right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nl}{\sqrt{Dt}} \right\} \quad (2)$$

Use of this equation gives a good first estimate of the diffusion coefficient of acid in the polymer film.

Figure 2 shows desorption data for trifluoroacetic acid diffusing in poly(hydroxystyrene) at 35°C. The x-axis of this plot is normalized to the film thickness since it represents data that were measured using two different films. The data show extremely good reproducibility.

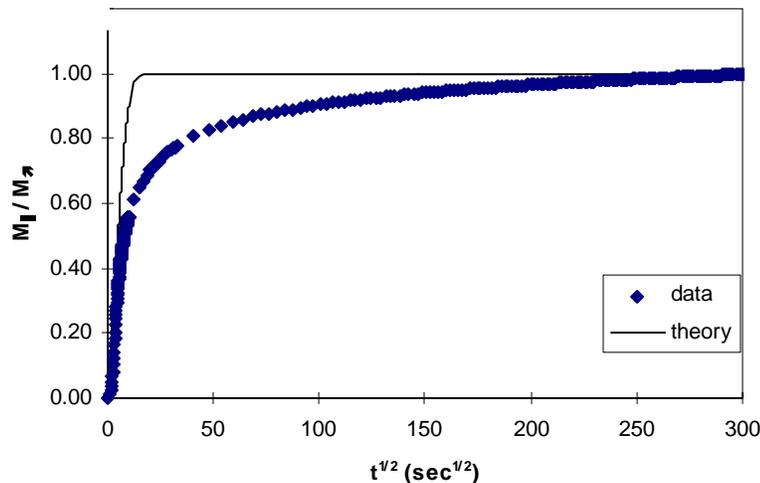


**Figure 2.** Trifluoroacetic acid desorption at 35°C

Figure 3 shows typical desorption plot for trifluoroacetic acid at 45°C. Table 1 shows the short-time diffusion coefficients that were calculated from these data.

**Table 1.** Diffusion coefficients for trifluoroacetic acid

Temperature (°C)	Diffusion Coefficient (cm <sup>2</sup> /sec)
35	$4.5 \times 10^{-10}$
45	$5.3 \times 10^{-10}$



**Figure 3.** Trifluoroacetic acid desorption at 45 °C

The equations given above do not fit the entire range of data as seen in Figure 3. This is probably because the diffusion coefficient is a strong function of concentration, and an expression is needed to take this into account. The equations given above (1-2) are for systems in which the diffusion coefficients are constant.

#### 4. Conclusions

This study has demonstrated that a quartz crystal microbalance can be used to measure the diffusion coefficients of acids in polymer films. Since the QCM has such high sensitivity for mass measurement, diffusion coefficients of thin films can be measured with accuracy. A significant amount of acid diffusion experiments still needs to be conducted for other acids which are of greater interest for chemically amplified resists. Included in this needed work is the determination of the dependence of the diffusion coefficients for these systems on acid concentration and on the extent of polymer blocking for CA resist systems.

## **5. Acknowledgments**

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