

# Dissolution Fundamentals of 193-nm Methacrylate Based Photoresists <sup>§</sup>

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## ABSTRACT

The dissolution of partially deprotected chemically amplified photoresists is the final step in printing lithographic features. Since this process step can be tuned independently from the design of the photoresist chemistry, measurements of the dissolution behavior may provide needed insights towards improving line-edge roughness. We have studied the dissolution behavior of a model 193-nm photoresist, poly (methyladamantyl methacrylate), as a function of deprotection extent and developer strength. The kinetics of the dissolution process is followed using the quartz crystal microbalance technique. These photoresist films exhibit strong swelling without dissolution over a significant range of deprotection levels. At larger extents of deprotection, we observe a combination of swelling with dissolution. Additionally, we find that the degree of film swelling decreases with tetramethylammonium hydroxide developer concentration. These studies provide the insight needed to better understand the fundamentals of the dissolution of the photoresist – a key step in lithographic process.

Keywords: dissolution, line edge roughness, photoresist, reflectivity, swelling

## INTRODUCTION

The process of imaging of patterns using photolithography relies on a change in solubility of the photoresist upon exposure to a light source.<sup>1</sup> For positive tone photoresists, polymer molecules in the exposed regions are rendered soluble by means of a chemical reaction which transforms hydrophobic moieties in the polymer chain. The diffusion of the photoacid within the polymer film leads to a polymer composition gradient at the line edge resulting in polymer molecules that are too hydrophobic to be rendered soluble in aqueous developer but are sufficiently hydrophilic to swell. This phenomenon of swelling at the line edge can have a significant effect on line edge roughness. In order to obtain a clearer understanding of the factors that control swelling, we have studied the swelling and dissolution of a model 193 nm photoresist as a function of deprotection extent, as well as developer concentration.

The response of deprotected photoresists upon exposure to an alkaline developer varies significantly with the photoresist chemistry. For example, novolac based photoresists are known to dissolve in developer solutions with minimal swelling<sup>2</sup> while the dissolution of methacrylate based photoresists is found to be preceded by significant swelling.<sup>3</sup> In the case of norborne based materials, the response of the polymer film has been found to be pH dependent with the polymer forming stable swollen layers at reduced Tetramethyl ammonium hydroxide (TMAH) concentration.<sup>4</sup> Such varied responses of the polymer films to the developer solutions have resulted in the postulation of different possible mechanisms of film dissolution.<sup>3,5,6</sup> In this paper, we show the effect of the processing dependent morphology on the swelling and dissolution of the polymer films.

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## EXPERIMENTAL METHODOLOGY<sup>#</sup>

### 1. Materials

Poly (methyladamantyl methacrylate) (pMAdMA) (weight average molecular weight ( $M_w$ ): 8800 g/mol, polydispersity index 1.18; DuPont) was dissolved in cyclohexanone (Aldrich, Reagent Grade) at a concentration of 5 % by mass. The photoacid generator (PAG), triphenylsulfonium perfluorobutanesulfonate (TPS-PFBS), was added at a loading of 2 % by mass of polymer. Since the PAG is light sensitive, amber vials wrapped in aluminum foil were used to minimize the exposure. The mixture was then heated to 55 °C for 30 minutes to ensure complete dissolution of the polymer. TMAH solutions were prepared by diluting a 25 % (by mass) stock solution (Aldrich) with deionized water purified and filtered by a Milli-Q system (Millipore) with final resistivity 18-M $\Omega$ -cm.

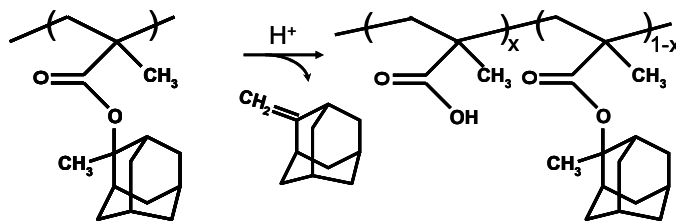


Figure 1. Acid catalyzed deprotection of PMAdMA.

### 2. Sample preparation

AT-cut quartz crystals (5 MHz, Q-Sense) with coating of silicon oxide or chromium were primed with hexamethyldisilazane (HMDS) to improve the adhesion of the polymer films to the surface. The QCM crystal was flooded with HMDS, heated for 90 s on a hotplate set at 150°C and after cooling to room temperature, rinsed with toluene. The water contact angles on the HMDS-primed substrates were typically 90°. Polymer films possessing a nominal thickness of 120 nm were obtained by spin coating the QCM substrates at 209 rad/s, followed by annealing at 130°C for 60 s in a convection oven. The films were then exposed to a broadband 248 nm filtered deuterium lamp (Oriel, 350 mW) for 30 s and baked at 90 °C for different times to obtain the variable degrees of deprotection in the polymer film. The deprotection mechanism shown in Figure 1 results in poly (methyladamantyl methacrylate-co-methacrylic acid) copolymer as well as residual fraction of methylene adamantane deprotection products

### 3. Infrared spectroscopy

The characterization of deprotection level and methylene adamantane residual level were performed in an external reflection mode on chromium coated quartz crystals. The deprotection reaction extent is quantified from the bending vibration mode of CH<sub>3</sub> (1360 cm<sup>-1</sup>) in the methyladamantyl group of PMAdMA. This band completely disappears and leaves a flat baseline if all the protected methyladamantyl methacrylate (MAdMA) groups are reacted. Additionally, this band also provides an absolute value of deprotection reaction and discriminates the residual methyleneadamantane products (MA) from the protected MAdMA group. The quantification of MA residual level is mainly based on the stretching vibration of H-C(=C) (3065cm<sup>-1</sup>) in the free MA molecule. Since pure MA was not commercially available, the calibration from IR absorbance of MA to its molar quantity can not be done directly. Instead, we use an indirect extrapolation method by assuming the MA is totally trapped if deprotection level is close to zero.

### 4. Quartz crystal microbalance (QCM) measurements

<sup>#</sup> Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

The response of the thin films exposed to varied aqueous solutions was measured by a quartz crystal microbalance (Q-Sense) with dissipation mode (QCM-D). The QCM-D setup follows the changes in the resonance frequency (5 MHz) as well as energy dissipation of the polymer coated quartz crystals upon exposure to TMAH solutions. This shift in the resonance frequency, measured as a function of time, was calculated relative to the resonance frequency of the coated crystal when immersed in water. For the polymer films used in this study, we were unable to accurately measure the shifts in the overtone frequencies (15, 25, and 35) MHz due to the rapid kinetics. Therefore, changes in the fundamental frequency of the quartz substrate will be presented in this paper. Qualitatively, for a polymer thin film, a drop in the resonance frequency of the quartz crystal upon exposure to developer can be associated with film swelling while an increase in the resonance frequency can be associated with mass loss. Film swelling will also lead to an increase in the measured energy dissipation from the film.<sup>7-10</sup>

## RESULTS AND DISCUSSION\*

### 1. Effect of copolymer composition by film processing

The kinetics of swelling and dissolution of the deprotected polymer films upon exposure to a 0.065 N TMAH solution are shown in Figure 2. Each of the plotted data set is an average of three independent QCM measurements. The swelling extent and kinetics are dependent upon the average methacrylic acid (MAA) fraction. At low methacrylic acid (MAA) fractions ( $f_{\text{MAA}} < 0.3$ ), there is no appreciable change in the values of  $\Delta F$ , indicating negligible solvent absorption by the polymer. As the MAA fraction of the copolymer film exceeds 0.3, there is an increase in the initial rate of change as well as in the extent of film swelling, as shown in Figure 2, between 0.31 and 0.60 mole fraction MAA. For polymer films with  $f_{\text{MAA}} > 0.7$ , the swelling process is accompanied by a mass loss from the polymer film. This can be seen most clearly in  $f_{\text{MAA}} = 0.74$  where the initial steep mass uptake is convoluted with an increasing frequency response; such a behavior is consistent with mass loss. However, in this measurement the two processes are convoluted; therefore the behavior appears as an initial swelling, followed by a partial film dissolution recovery. The dissolution rate, of the polymer films increases with increasing MAA content with most of the film dissolving when  $f_{\text{MAA}}$  exceed 0.78. The swelling and dissolution process also leads to a qualitative change in the viscoelastic properties of the polymer film. These viscoelastic properties are observed from changes in the energy dissipation ( $\Delta D$ ) within the film as shown in Figure 3. While the energy dissipation increases as the films swell, the onset of dissolution leads to a drop in the dissipation.

In Figure 4, we show the limiting values of the resonance frequency,  $\Delta F$ , as well as the dissipation  $\Delta D$  of the polymer coated substrates as a function of the average MAA content. The quasi-equilibrium response of the film upon exposure to the developer solution may be separated into four distinct regimes corresponding to (I) no swelling ( $0 < f_{\text{MAA}} < 0.3$ ), (II) swelling only ( $0.3 < f_{\text{MAA}} < 0.5$ ), (III) partial dissolution ( $0.5 < f_{\text{MAA}} < 0.7$ ) and (IV) complete dissolution ( $f_{\text{MAA}} > 0.7$ ). This response of the polymer upon exposure to the developer solution at different deprotection levels can be explained as follows. Poly (methyladamantyl methacrylate) is very hydrophobic and does not swell or dissolve in water or hydroxide solution. However, the conversion of this polymer into a poly (methyladamantyl methacrylate-co-methacrylic acid) copolymer introduces a hydrophilic character to the material. The different responses of the polymer film to the developer solution are a consequence of the increasing hydrophilicity of the polymer film. Since the desired polymer composition and morphology is determined by the means of an *in situ* reaction, we first discuss the effect of the processing conditions on the distribution of the methacrylic acid moieties within the film.

At short bake times, the polymer morphology can be as described as a hydrophobic continuum with a random dispersion of reaction domains composed of hydrophilic methacrylic acid groups. Such a scheme was found experimentally under conditions of very dilute domain conditions.<sup>11</sup> At this early stage, the hydrophobic character of the polymer prevents penetration of water into the film because individual methacrylic acid moieties are inaccessible (regime I). As the methacrylic acid content of the polymer film increases due to the diffusion and reaction of the photoacid, these groups form a percolated hydrophilic network within the hydrophobic matrix. It is the percolated character of these groups that provides a pathway for transport of hydroxide ions into the film thereby resulting in

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\* The data throughout the manuscript and the figures are presented along with the standard uncertainty ( $\pm$ ) involved in the measurement based on one standard deviation

film swelling. The onset of film swelling in our system corresponds to a methacrylic acid fraction of 0.3 which is remarkably close to the site percolation threshold of a simple cubic lattice. Beyond this percolation threshold, increasing the methacrylic acid content of the polymer increases the rate of swelling, as well as the total mass uptake in Figure 4. Such an effect can be attributed to the increasing hydrophilic nature of the polymer film. The decrease

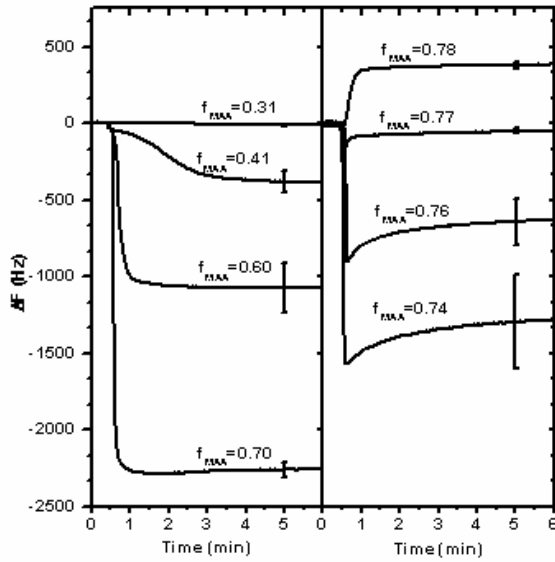


Figure 2: Change in the resonance frequency of polymer coated quartz crystals when exposed to a 0.065 N TMAH solution

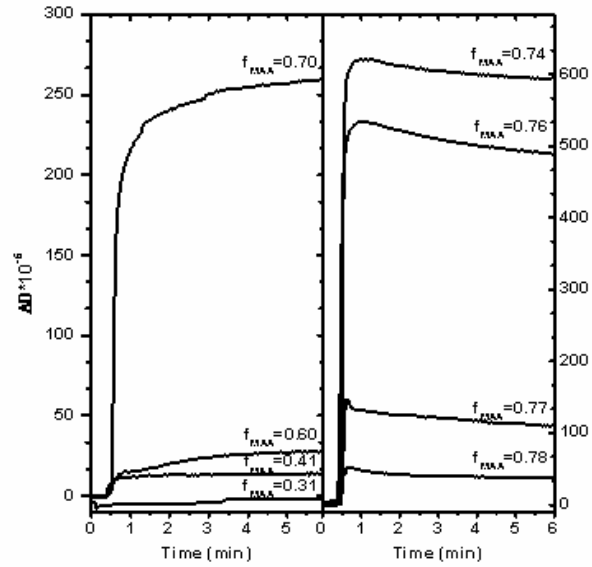


Figure 3: Change in the energy dissipation of polymer coated quartz crystals when exposed to a 0.065 N TMAH solution

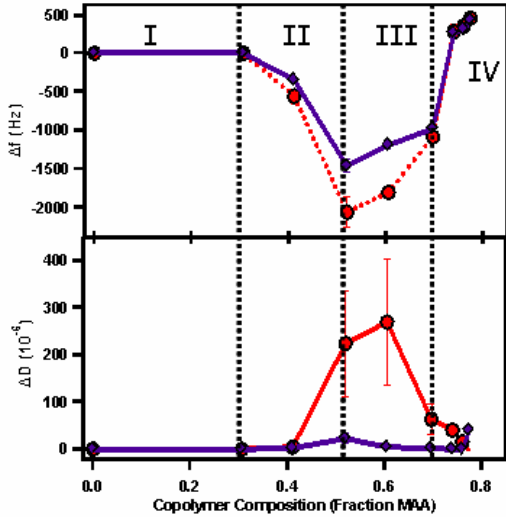


Figure 4: Changes in the resonance frequency and energy dissipation of the polymer coated quartz crystals upon equilibration in 0.01 N (circles) and 0.26 N (diamonds) TMAH solutions. The solid lines are a guide to the eye

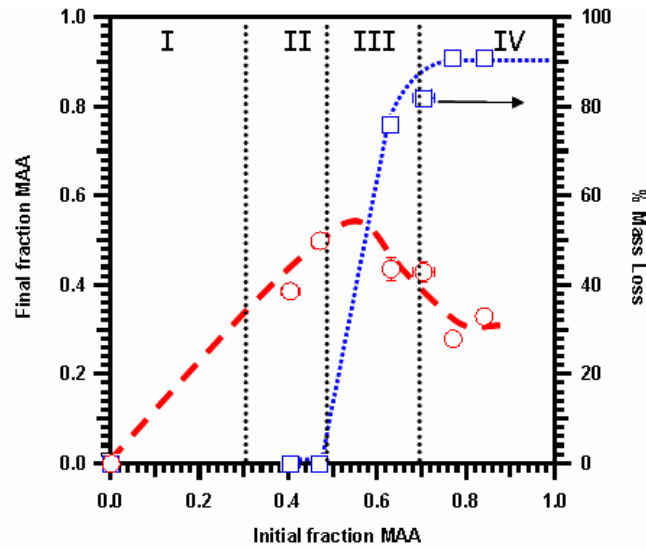


Figure 5: Change in composition (circles) of the polymer film upon exposure to 0.26 N TMAH solution. The corresponding change in the total polymer content (squares) is plotted on the right axis. The solid lines are a guide to the eye

in values of  $\Delta F$  as the methacrylic acid fraction exceeds 0.5 is due to the dissolution of the polymer chains from the swollen layer. Ideally, the copolymer molecules should be rendered soluble when the methacrylic acid content

exceeds a critical value. The switch in the solubility of our polymer films occurs gradually and dissolution proceeds via the expulsion of polymer chains from the swollen matrix. The number of chains being expelled from the matrix increases with increasing methacrylic acid content. Since we expect heterogeneity in the local copolymer composition, these observations can be explained by the following mechanism. As the average composition of the copolymer film approaches the solubility switch, chains with methacrylic acid contents exceeding the solubility switch will escape from the swollen matrix (regime III in Figure 4). With increasing deprotection extents, the relative fraction of soluble chains increases, at the expense of the hydrophobic matrix. Eventually the film dissolves faster than it swells which corresponds to regime IV in Figure 4.

Spectroscopic analysis of the film composition after exposure to 0.26N TMAH solution provides further insight to the development process. In Figure 5, we have plotted the change in mass as well as the composition of the polymer film after development as a function of the initial methacrylic acid content. From the data in Figure 5, it is clear that in regime I and II, the film composition as well as the total polymer content do not change upon exposure to TMAH. Such an observation is consistent with the hypothesis of swelling only behavior of the polymer film. This hypothesis of polymer chains dissolving from a matrix (regime III) is confirmed by the drop in the average methacrylic acid content of the polymer film after exposure to a 0.26N TMAH solution). Finally, in regime IV, we find that there exists a residual layer whose methacrylic acid content is near 30 %. The origins of this layer are unclear at the present time.

## **2. Effect of developer strength**

The data in Figure 4 show that the swelling of the polymer films is greater in 0.01 N TMAH as compared to a 0.26 N TMAH solution. To obtain a better understanding of this phenomenon, we studied the swelling of polymer films as a function of TMAH concentration at three different copolymer compositions with the methacrylic acid fraction ranging from 0.4 to 0.6. The changes in  $\Delta F$  and  $\Delta D$  of these films upon equilibration are plotted in Figure 6. In the case of copolymer films containing 41 % methacrylic acid,  $\Delta F$  and  $\Delta D$  exhibit a weak dependence on the developer concentration indicating that the extent of film swelling at this composition does not depend upon the developer strength. However, as the average methacrylic acid content of the film increases, the dependence of  $\Delta F$  and  $\Delta D$  on the developer strength becomes more pronounced. For polymer films containing (52 and 60) % MAA, the largest change in  $\Delta F$  and  $\Delta D$  is observed at the lowest developer concentration (0.01 N) used in this study. Additionally,  $\Delta D$  decreases sharply with increasing developer strength.

These observations can be explained on the basis of increased screening of the electrostatic interactions between the titrated methacrylic acid groups (pKa of 7.2) by TMAH. At a TMAH concentration of 0.01N, the polymer films are completely ionized, and the subsequent electrostatic repulsions between the ionized groups results in the formation of a highly swollen film with low values of shear viscosity as well as low shear elastic modulus. With increasing TMAH concentration, sorption of additional TMAH into the polymer film results in the screening of the electrostatic repulsion between the ionized groups of the polymer chains. The aforementioned charge screening will result in a reduction in the extent of film swelling. The resulting increase in the local polymer concentration within the swollen film leads to an increase in the values of shear viscosity and elastic storage modulus resulting in a decrease in the values of  $\Delta D$  such as those observed in Figure 6.

## **CONCLUSIONS**

We have characterized the swelling and dissolution of poly (methyladamantyl methacrylate-co-methacrylic acid) thin films in aqueous TMAH solutions as a function of copolymer composition as well as TMAH concentration. The onset of film swelling can be explained on the basis of a percolation framework with film swelling observed when the methacrylic acid fraction exceeds 0.3. The extents of swelling as well as the swelling rate depend upon the copolymer composition as well as TMAH concentration. Increasing the TMAH concentration increases the swelling rate, but the increase in the local TMAH concentration results in the screening of electrostatic interactions between the ionized methacrylic acid groups resulting in a drop in the extent of film swelling.

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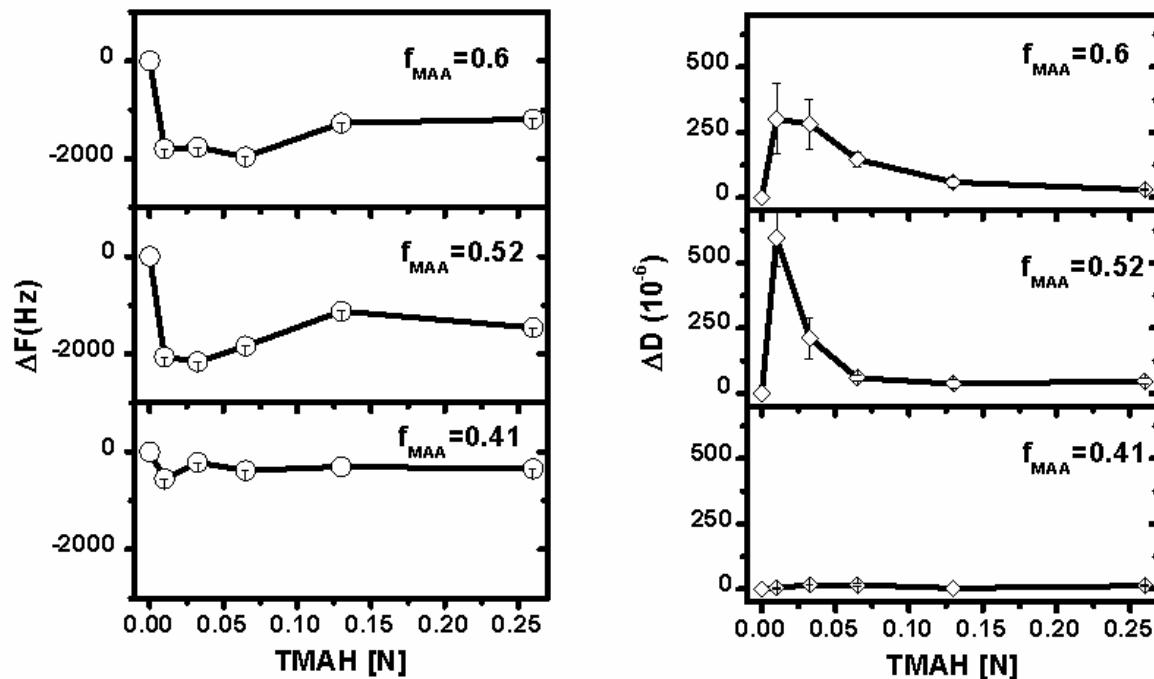


Figure 6: Swelling of polymer films as a function of developer strength. The plots show the changes in the resonance frequency ( $\Delta F$ ) and dissipation ( $\Delta D$ ) as a function of TMAH concentration for three copolymer compositions. The solid lines are a guide to the eye

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