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The effect of humidity on water sorption in photoresist polymer thin films

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Abstract

A quartz crystal microbalance technique has been utilized to measure water sorption and desorption in three photoresist polymers: poly(*p*-hydroxystyrene), novolac, and bis-triflouromethyl carbinol substituted poly(norbornene). The humidity of the sample environment was varied to determine the rate and amount of water absorbed into the photoresist thin films as a function of local environmental conditions. At 100% absolute humidity, the polymers were found to absorb 9.8, 2–3, and 5–8 wt%, respectively. The sorption and diffusion of water into the polymer thin films was observed to initially follow Fickian behavior in the low fractional mass uptake regions ($M_t/M_\infty < 0.6$), but concentration dependent diffusion behavior was seen at higher levels of water uptake. All films sorbed and desorbed water rapidly with the majority of the water uptake or loss occurring in the first few seconds of exposure.

Keywords: Sorption; Photoresist; Quartz crystal microbalance

1. Introduction

The presence of small amounts of water in polymer thin films has previously been shown to affect a variety of thin film physical properties. These effects range from altering mechanical properties [1,2] such as tensile stress or hardness, to changing electronic properties such as the net dielectric constant of the film [3–5]. There can also be a variety of special situations where the presence or lack of water in a polymer can alter the chemistry and processing of polymer thin films. For example, the semiconductor industry utilizes polymer thin films known as photoresists in the fabrication of integrated circuits. These materials undergo chemical changes upon exposure to light that render the polymer film more or less soluble in a developer solution, thus making it possible to generate three-dimensional relief images in the polymer film. These polymer relief images act as protective masks during various etch processes and serve to protect the underlying substrate layers from damage. The presence or lack of water in a photoresist film can change the physical and chemical properties of the resist film and thus alter the imaging characteristics of the resist. In particular, the amount of water in a resist film can affect the reaction pathways responsible for the solubility changes that permit lithographic imaging of the materials. For example, in traditional diazonaphthoquinone-novolac (DNQ-novolac) photoresists, the presence of water in the film is necessary for proper conversion of the diazonaphthoquinone (DNQ) to its desired carboxylic acid product form. Too little water in the resist film during exposure can lead to undesired side reactions between the photoactive DNQ dissolution inhibitor and the novolac resin. These side reactions generally result in significant degradations in the lithographic performance of the resist [6]. Similar issues can be found in modern chemically amplified resists as well. Burns et al. demonstrated that changes in relative humidity can influence the rates of deprotection and acid transport in a chemically amplified resist [7,8]. Finally, water's presence in the polymer thin film could potentially alter the absorbance characteristics of the resist polymer leading to degradation of image quality. At 157 nm, the extinction coefficient of water is approximately 0.218 which corresponds to an absorbance of 17.5 μm^{-1} for pure water [9]. This value translates into water essentially being opaque to radiation at 157 nm wavelengths. If the lithography process and time scale for water desorption from the resist film are such that even relatively small amounts of water are retained in the resist film during the exposure process, the net absorbance of the resist polymer could be increased significantly. This

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increased resist absorbance would in turn result in serious degradations in imaging performance. Therefore, it is particularly important to understand both the amount of water absorbed into the polymer film at a given set of environmental conditions and also the rate at which the water content changes.

Due to this ability of water to dramatically affect thin film properties and performance, it is very important to understand how environmental conditions affect the rate and extent of water uptake in polymer thin films. Surprisingly, relatively little information has previously been published regarding water sorption in photoresist thin films [2,7,8,10–13]. It was the goal of this work to establish a methodology and to obtain reliable water sorption data for a series of common polymers used in modern photoresists, poly(*p*-hydroxystyrene) (PHOST), novolac, and bis-trifluoromethyl carbinol substituted polynorbornene (HFAPNB). These first two materials are the basis of DUV (248 nm) and I-line (365 nm) resist materials, respectively. The last material, bis-trifluoromethyl carbinol substituted polynorbornene (HFAPNB), is a model homopolymer for fluorinated resist material architectures that may be used in 157 nm lithography.

There have been many methods used to measure water sorption in polymer films. These include gas permeation techniques [14–17], electro-microbalances [14–17], quartz spring microbalances [18–20], FTIR [21], and stress analyzers [22–24]. The method utilized in these experiments examines the shift in resonant frequency of a quartz crystal microbalance (QCM) as mass (i.e. water) is added to a polymer film coated onto the crystal surface.

2. Experimental

2.1. Materials and Sample Preparation

A series of electronic grade photoresist resin polymers were obtained from commercial electronic material suppliers as follows: PHOST ($M_w = 11,800$) was obtained from Triquest Chemical Company; novolac sample #1 ($M_w = 1,615$, PDI = 2.283) was obtained from Shipley Company; novolac sample #2 ($M_w \approx 22,000$, PDI $\approx$ 25) was obtained from AZ Electronic Materials, and two HFAPNB resins (HFAPNB-1: $M_w = 8,882$, PDI = 2.25 and HFAPNB-2: $M_w = 94,159$, PDI = 9.21) were obtained from Promerus Electronic Materials. Fig. 1 shows the generic structure of all three polymer types. Both the HFAPNB and PHOST samples are known to be linear homopolymers. In the case of novolacs, it is common to polymerize mixtures of *meta*- and *para*-cresols with small amounts of other comonomers that introduce some degree of branching in the material. Such detailed structural information for the novolac samples used in this work is not available. Ethyl lactate (98%) and propylene glycol methyl ether acetate (PGMEA) (99%) were purchased from Aldrich Chemical Co. and used as

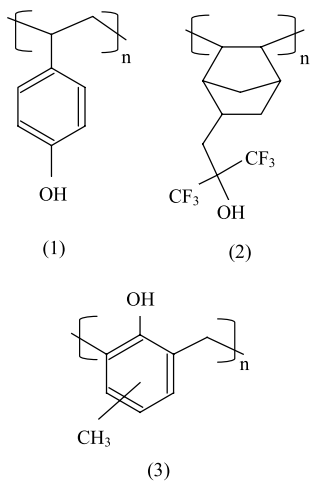

Fig. 1. Chemical structure of (1) PHOST, (2) HFAPNB, (3) Novolac.

casting solvents for the various polymers. The polymers and solvent were used as received.

PHOST was dissolved in ethyl lactate to create a polymer solution containing 13.2 wt% solids. The solution was then filtered through 0.2 μm teflon filters and spin-coated at 1000 rpm for 30 s onto QCM crystals using a CEE Model 100 CB spin coat and bake system to create films approximately 1.1 μm in thickness. A soft bake of 115 °C for 3 min was performed to remove the majority of residual casting solvent left in the film after spin coating.

Novolac samples #1 and #2 were dissolved in PGMEA to create 14.8 and 19.8 wt% solutions, respectively. Both resin solutions were filtered and spin coated at 1000 rpm for 30 s to create films approximately 0.8 and 1.4 μm thick, respectively. All novolac films were soft baked at 115 °C for 3 min to remove residual casting solvent.

The HFAPNB-1 and HFAPNB-2 samples were dissolved in PGMEA to create 24.9 and 15.7 wt% solutions, respectively. Both solutions were filtered and spin coated at 2000 rpm for 30 s to create films 1.1 and 0.6 μm thick, respectively. All HFAPNB films were soft baked at 115°C for 3 minutes to remove residual casting solvent.

2.2. Film thickness measurement

A V-Vase variable angle spectroscopic ellipsometer (J.A. Woollam Inc.) was used to measure the thickness of the cast polymer films. The ellipsometry parameters, Ψ and Δ were collected over the wavelength range from 500 to 1000 nm at angles of 65, 70, and 75°. The Ψ and Δ data were analyzed using the WVASE-32 analysis software (J.A. Woollam Inc.) by fitting the ellipsometry data using a film stack model composed of a Cauchy layer model for the polymer film and a semi-infinite gold film for the substrate.

2.3. Water sorption measurements

Two small humidity chambers were custom designed and

constructed for this work. Nitrogen gas from the head space of a liquid N_2 cylinder was used to purge the chambers and provide a low humidity environment. A nitrogen gas and/or room air stream was bubbled through a small water reservoir and introduced into the chamber in order to adjust the humidity level. The humidity in the chamber could be controlled by adjusting the flow rate of gas passed through the water bubbler. A hygrometer probe (Omega, model # RH411) was inserted into the chamber near the location of the polymer coated samples and used to provide real-time monitoring of relative humidity.

A Maxtek QCM (PLO-10 Phase Lock Oscillator, 5 MHz gold plated quartz crystals model # SC-501-1, 1.227 cm^2 active area) was used to measure the uptake of water into the polymer films by measuring the shift in QCM oscillator frequency as water was sorbed into and desorbed from the polymer coated crystal.

Initially, the coated crystals were allowed to reach equilibrium at room humidity conditions (49–55% relative humidity during the period of these experiments) outside of the humidity chambers. During this time, one humidity chamber was allowed to stabilize at a low humidity value (6–9%) while the other stabilized at a high humidity value (93–98%). The dynamics of water sorption in the various films was investigated by monitoring water sorption and desorption from the films as they were transferred from one chamber to the other. First, the QCM crystal and holder was placed inside the low humidity chamber and allowed to equilibrate. The frequency of the QCM crystal was recorded as the film desorbed water. Once the frequency of the QCM crystal stabilized at the low humidity value the crystal was transferred immediately into the high humidity chamber and the crystal frequency was recorded as the film sorbed water. After stabilizing at the high humidity value, the crystal was transferred back into the low humidity environment and the crystal frequency was again recorded as the film desorbed water. This process was repeated several times to investigate the reproducibility of the data. Static equilibrium crystal frequency values were also measured for intermediate humidity values by adjusting the humidity of one of the humidity chambers and allowing the coated crystal to equilibrate in the chamber at each desired humidity level. These equilibrium frequency values for each humidity were recorded and used to determine a relationship between mass of water absorbed and humidity. The temperature inside the chamber was held relatively constant at 22.8 ± 1.2 °C during all of these experiments.

3. Results and discussion

3.1. Total water uptake

The effect of ambient relative humidity on water sorption in photoresist thin films was investigated by measuring the frequency shift of polymer coated QCM crystals exposed to varying relative humidity environments. The frequency versus relative humidity data was then used to calculate a relationship between water mass in the thin film versus water partial pressure in the environment.

Obtaining the water partial pressure is a simple calculation that only requires knowledge of the water vapor pressure at the experimental temperature of 22.8 °C (20.777 mm Hg) and the relative humidity in the environment. Relative humidity is the partial pressure of water divided by the vapor pressure of water. Thus to obtain the partial pressure of water one has to simply multiply the relative humidity by the vapor pressure of water.

The next step in obtaining water uptake versus water partial pressure was to convert the QCM frequency data into mass or percent water uptake. Initially, the frequency data was plotted against water partial pressure and a linear least squares fit was used to model the data as illustrated for the HFAPNB-2 sample shown in Fig. 2. As can be seen from Fig. 2, this linear fit captures the trend in the data well with an R^2 value of approximately 0.97. The intercept of this linear fit should in principle be the frequency of the film coated crystal in a completely dry environment, and thus it is used to calculate the 'dry' mass of the polymer thin film. It should be noted that it is quite possible that there are small quantities of water tightly bound to the polymer matrices that would remain in the film even in completely dry environments. Thus the absolute dry mass of the polymer film may be slightly lower than that calculated from the method used here. For the purposes of this work, the calculated dry mass is used to estimate the overall mass gain due to water sorption rather than actual water content of the film. The water content values reported here are probably reasonable estimates of actual water content, however, it should be noted that the actual total water content in the materials may be slightly higher than that reported in this paper due to the effect of bound water.

The natural frequency of the QCM crystal used in each experiment was measured before being coated with the polymer film. The mass of material on the crystal can then

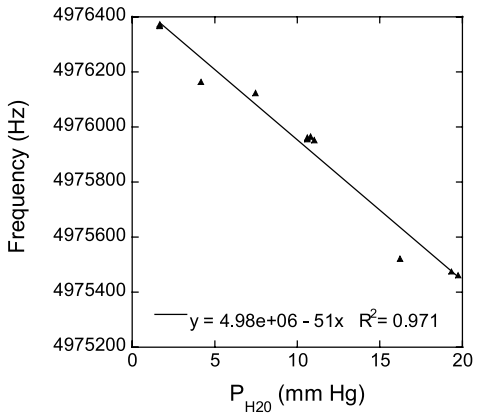

Fig. 2. QCM frequency versus water partial pressure for HFAPNB-1.

be calculated using Eq. (1) which is simply a variation of the Sauerbrey equation [25]

$$m_{\text{added}} = \frac{(f_{\text{uncoated}} - f_{\text{measured}})}{C_f} \quad (1)$$

In this equation, m_{added} is the mass added to the crystal per unit area, f_{uncoated} is the natural frequency of the clean crystal, f_{measured} is the frequency of the crystal after some mass is added to the crystal, and C_f is a constant calculated using Eq. (2) [25]

$$C_f = \frac{2f_q^2}{(\rho_q v_q)} \quad (2)$$

Here f_q is the resonant frequency of the bare crystal (nominally 5.0 MHz), ρ_q is the density of the quartz crystal (2.649 g/cm^3), and v_q is the shear wave velocity of the AT cut quartz crystals used in this study (332,200 cm/s). It is important to note that the Sauerbrey equation is only valid for thin films that can be considered rigid masses. If the film is not a rigid mass, the shear wave in the QCM crystal will propagate into the coated film and lose a significant amount of energy. This energy loss will in turn affect the frequency measurement and the crystal behavior can deviate strongly from the Sauerbrey relationship. The rigid mass requirement for the Sauerbrey equation is especially important for high mass loadings on the QCM crystal. A good indicator of the elastic behavior of the quartz crystal/polymer film system is the ratio of the acoustic impedance (Z) of the respective materials [25]. As the elastic behavior of the polymer film changes, the value of Z will change as well. It has been shown that for high mass loadings on a QCM significant deviations from the Sauerbrey equation can occur for small changes in Z [25]. This could mean the potential for calculation errors as water is absorbed into the polymer films, plasticizes them, and changes their elastic behavior (Z value). Fortunately, any changes in the elastic behavior of the polymer films studied in this paper should not create a significant deviation from the Sauerbrey equation. This statement is supported by the fact that while demonstrating the effect of changing Z at high mass loadings created significant measurement errors, it was also shown that at low mass loadings or crystal frequency shifts, (i.e. delta frequency due to mass addition divided by crystal resonant frequency is less than 0.05) that the mass/frequency relationships for all values of Z will converge upon the Sauerbrey relationship [25]. The frequency shift ratios observed in the experiments reported here were very small (0.001–0.002), and thus the use of the Sauerbrey relationship to calculate mass added to the crystal from the crystal's frequency shift should introduce insignificant error.

Using Eqs. (1) and (2) it is possible to calculate equilibrium water uptake data for various water partial pressures. Fig. 3 shows this data for all five polymer samples studied in this work. As expected, the water content of the polymer films increases with increasing ambient water content. In fact, in this case the water uptake exhibits a linear relationship with water partial pressure over the entire range of measured polymer water contents, similar in nature to that observed for ideal liquid–vapor systems described by Henry's Law.

Table 1 lists the equilibrium water uptake in a saturated environment for these polymers. All three polymer types used in this study contain hydroxyl functional groups that are hydrophilic and capable of hydrogen bonding to some degree with sorbed water molecules. Due to the hydrophilic nature of these groups, all of the polymers are capable of absorbing significant quantities of water. Nevertheless, there are sharp differences in the amount of water sorbed between the novolac resins (~ 2–3 wt%), HFAPNB resins (~ 5–8 wt%), and the PHOST (9–10 wt%). This difference in the amount of water sorbed in these materials can be a result of various factors including free volume differences between the materials and differences in the affinity or solubility of water in the polymers. Based on knowledge of the behavior of these polymers in their use as photoresist resins, it is believed that one contributor to these differences in water uptake is the ability of these polymers to exhibit hydrogen bonding between hydroxyl groups on the same polymer chain or between chains. Such hydrogen bonding could then effectively reduce the ability of these hydroxyl groups to bind to as many or as strongly to sorbed water molecules, thus lowering the capacity of the polymer to absorb water. Novolac and HFAPNB polymers are known to form hydrogen bonds between hydroxyl groups adjacent to one another on the same polymer chain or on neighboring chains [6,26], while little evidence has been found for hydrogen bonding in polyhydroxystyrene matrices. This fact is supported by the ability of researchers to develop dissolution inhibitors that function through hydrogen bonding for HFAPNB type materials and novolac, while attempts to make such inhibitors for polyhydroxystyrene have been unsuccessful [6,26,27].

In order to further test this hypothesis, water sorption in two different molecular weight HFAPNB polymers was measured. HFAPNB-1 had a low molecular weight of 8,882 while HFAPNB-2 had a much higher molecular weight of 94,159. It is known that the PNB materials used in this work, which were made using Pd catalysts, form an unusual rigid-rod like helix-kink morphology [26,28]. This polymer secondary structure results in a number of unusual physical properties for these materials. As the molecular weight of the HFAPNB is increased, it has been observed through Fourier transform infrared spectroscopy studies that the level of hydrogen bonding in thin films of this material decreases. Therefore, one might expect the amount of water uptake in higher molecular weight HFAPNB polymers to increase as the molecular weight of the material increases. Thus, the ultimate equilibrium water uptake for HFAPNB-2 was expected to be higher than

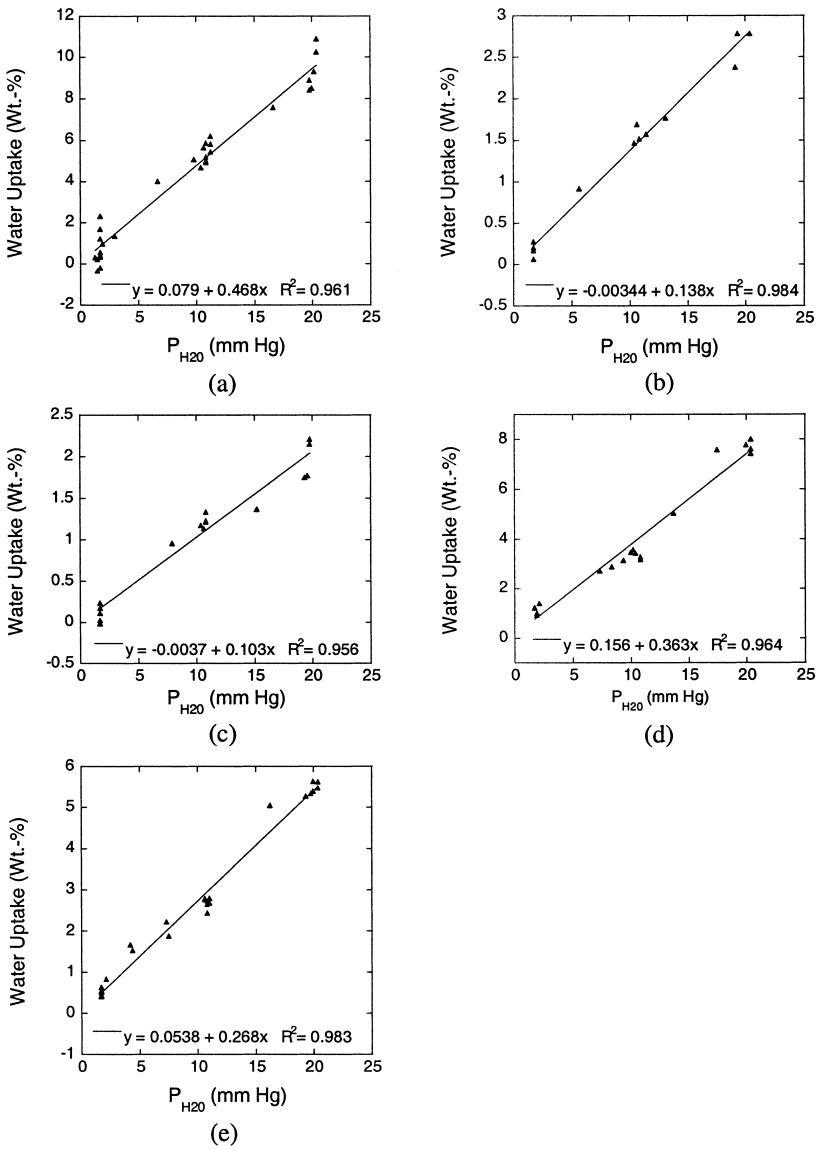

Fig. 3. Equilibrium water uptake data for (a) PHOST, (b) novolac #2, (c) novolac #1, (d) HFAPNB-2, (e) HFAPNB-1.

that of HFAPNB-1. As illustrated in Table 1, this increase in water uptake with molecular weight has been observed. The higher molecular weight HFAPNB absorbed 7.7 wt% while the lower molecular weight version absorbed only 5.6 wt%. It should be pointed out that this increase in molecular weight for the HFAPNB films may also result in a slight increase in the polymer free volume, which may also contribute to this increase in the polymer's ability to absorb water.

3.2. Diffusion behavior

The dynamic frequency data was examined to determine the rates of water absorption and diffusion during the

Table 1
Water sorption data for all polymer samples

Polymer	Molecular weight	Maximum water uptake (wt%)	Estimated diffusion coefficient ($\times 10^{-09}$ cm^2/s) for water sorption
PHOST	11,800	9.8	1.8
HFAPNB-1	8,882	5.6	3.5
HFAPNB-2	94,159	7.7	1.9
Novolac-1	1,615	2.2	0.31
Novolac-2	~22,000	2.9	0.28

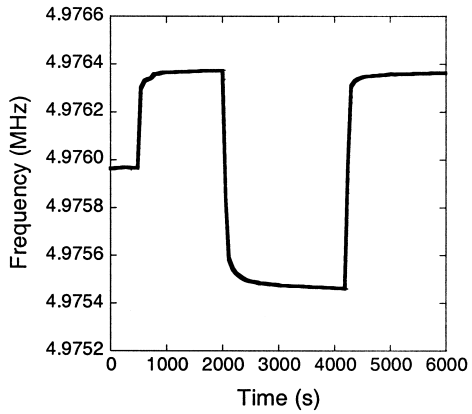

Fig. 4. Typical raw data for the QCM frequency response to sorption/desorption.

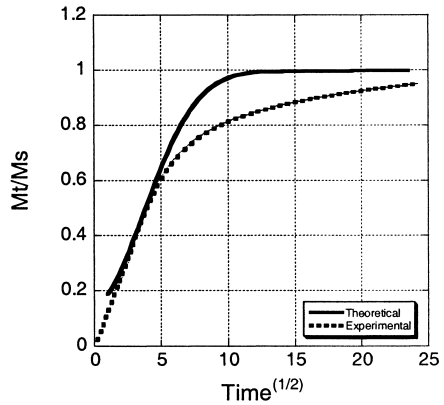

Fig. 5. Comparison of Fickian predicted fractional mass uptake to observed experimental mass uptake (time units used are in seconds).

sorption and desorption experiments. Fig. 4 illustrates a typical set of sorption–desorption frequency data from these experiments. In all cases, the frequency data indicated that qualitatively the sorption–desorption processes are quite rapid, with the majority of the water gain or loss occurring during the first few seconds after the environmental conditions are changed. In fact, all polymers sorbed at least 80% of their final equilibrium water uptake within the first 3 min of exposure to the more humid environment.

If purely Fickian diffusion was occurring during these processes, the diffusion behavior and water uptake could be modeled using the following equation [2,29–34]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2 Dt}{L^2}\right] \quad (3)$$

where M_t is the mass uptake at time t, M_∞ is the ultimate mass uptake at time $t = \infty$, D is the diffusion coefficient (cm^2/s), and L is the film thickness. For the initial phases of the sorption process ($M_t/M_\infty < 0.6$), the water uptake for these polymers is observed to follow a linear relationship versus the square root of time as would be expected for a Fickian diffusion process. Thus, a simplified version of Eq. (3) can be used that describes mass uptake into a thin, semi-infinite slab from one face [1,29,33–35]

$$\frac{M_t}{M_\infty} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{1/2} \quad (4)$$

This equation is often referred to as the 'short time' equation and was used to estimate a Fickian diffusion coefficient of the various polymers studied. Fractional mass uptake (M_t/M_∞) was plotted against $t^{1/2}$ and the slope of the resulting plot was used to evaluate D. Fig. 5 shows the fractional mass uptake versus the square root of time for novolac sample #2, which is typical for the polymers studied in this work.

Table 1 lists the estimated Fickian diffusion coefficient values for the polymers studied in this work. These diffusion coefficients are applicable generally for water uptake values where $M_t/M_\infty < 0.6$. PHOST and the HFANB polymers absorbed water quite rapidly with diffusion coefficient values between 1.8×10^{-9} and 3.5×10^{-9} cm^2/s. The novolac resins were somewhat slower with values near 0.3×10^{-9} cm^2/s.

It is interesting to note that the estimated diffusion coefficient for the novolac resins (0.3×10^{-9} cm^2/s) is somewhat smaller than that found in previous work with novolac resist systems ($1.0–1.3 \times 10^{-9}$ cm^2/s) [11–13]. Though it is not certain, it is possible that this difference in diffusion rate is due to differences in composition of the novolac materials studied. In particular, each of the three previous studies examined water sorption in commercial positive type novolac resists (AZP4620 and AZ 9260 from Clariant [11], HPR 204 from Hunt Chemical [12], and OFPR 800 from Tokyo Ohka Kogyo [13]). In addition to the novolac matrix polymer, these systems are undoubtedly loaded with a sensitizer compound (most likely some form of diazonapthoquinone dissolution rate inhibitor) and other dissolution rate modifiers. The system studied here consisted only of a pure novolac polymer matrix (i.e. no sensitizers or other additives) cast from a single solvent. It is likely that these additives could be partly responsible for the faster diffusion observed in the commercial resists. For example, it is possible that the DNQ and other additives may act as plasticizers and allow for faster rates of diffusion. It is also possible that film additives and variations in the film preparation conditions could lead to varying amounts of residual casting solvent in the film. Such film composition and thermal history differences could also then lead to changes in the diffusion behavior of the films due to plasticization and other effects.

As seen in Fig. 5, the fractional mass uptake data exhibited Fickian diffusion behavior in the initial short time phases of the sorption process. This is indicated by the initially linear trend in mass uptake versus the square root of time. Fickian behavior in the initial short times was observed in all of the polymers examined. Fig. 5 also illustrates theoretical Fickian mass uptake calculated from Eq. (3) using the short time Fickian diffusion coefficient

found for that particular novolac sample. Obviously a significant deviation from Fickian diffusion occurs at high mass uptake values. This type of deviation was observed to varying degrees for all of the polymers used in this work and is indicative of a concentration dependent diffusion coefficient [31,33].

As seen in Fig. 5, the sorption data for both the novolac and polynorbornene materials displayed a smooth gradual transition from the linear sorption region (Fickian regime) into the final non-Fickian equilibration regions. The data for PHOST was somewhat different, showing a sharp slowing in the rate of sorption at total percent mass uptakes of approximately 65–70%. Fig. 6 shows a close-up view of the region in the PHOST sorption versus time curve where this phenomenon occurs for a representative data set. Using mass ratio data, this level of water uptake corresponds to the point where one water molecule is present per every two hydroxyl groups in the PHOST. Thus, this sharp transition may represent the point at which direct hydrogen bonding of water molecules with the polymer are virtually exhausted. At this point, the penetrant water molecules are likely to be found hydrogen bonding with one another to form clusters.

4. Conclusions

Water sorption data were collected for five different polymers at various relative humidity values. Based on the frequency data collected from the QCM system, a number of conclusions can be drawn. First, a linear relationship was found for water uptake versus water partial pressure for all polymers studied. All polymers absorbed significant quantities of water in a saturated environment with PHOST absorbing the most (9.8 wt%) followed by high molecular weight HFANB (7.7 wt%), low molecular weight HFANB (5.6 wt%), and the novolac resins (2–3 wt%). The ability of hydroxyl groups on the polymer to hydrogen bond with water is suspected to play a major role in the ability of the polymer to absorb water. Second, the rates of sorption and desorption in all of the polymers studied were rapid, with the majority of the water uptake occurring within the first few seconds of exposure to the humid environment. Finally, the diffusion of water into the polymers at low water uptakes (i.e. $M_t/M_\infty < 0.6$) followed Fickian behavior as exhibited by the linear relationship between fractional mass uptake and the square root of time for these materials. At high mass uptake values, all polymers deviated from Fickian behavior and exhibited trends indicative of concentration dependent diffusion.

The experiments performed in this study were all conducted at or near room temperature. Often in lithography processing, resist films are subjected to elevated temperature sequences such as post- apply or post-exposure bakes. It would be expected that the diffusion rate of water and other solvents in the films would be higher at elevated temperatures. In fact, the post-apply bake is performed for exactly this reason, with the goal being to quickly remove solvent by using these enhanced diffusion rates. The effect that elevated temperature processing would have upon equilibrium water content is a little less clear. Previous work by others regarding sorption of water into epoxy and epoxy/carbon fiber composites has indicated that the equilibrium water content increases with increasing temperature [36]. Experiments to examine the effects of baking conditions upon water uptake in resist polymer films are in progress.

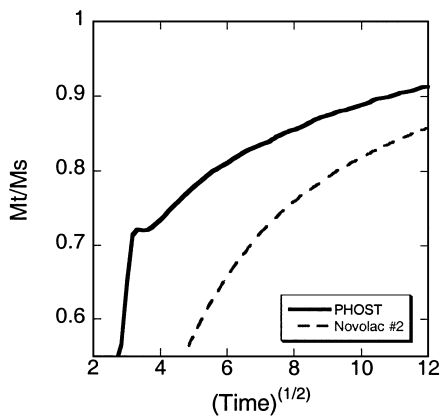

Fig. 6. Comparison of PHOST and novolac sorption curves at large extents of water uptake (time units are in seconds).

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