MEASUREMENT OF ACID DIFFUSIVITY IN THIN POLYMER FILMS ABOVE AND BELOW Tg

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Introduction

Most advanced photoresists used in the manufacture of microelectronic devices rely on the principle of chemical-amplification. Rather than using light to directly cause a solubility switch, chemically amplified photoresists use light only to generate a catalytic species. The photo-generated catalyst, typically an acid, then promotes a solubility switching chemical reaction in the exposed regions of the photoresist. The resulting latent image can then be developed and transferred into the underlying substrate.

While chemically amplified resists have many advantages, one inherent limitation is catalyst diffusion. That is, catalyst generated in exposed regions can potentially diffuse into unexposed regions, thus causing line-width spread or image blur. This blurring effect is an observed fact in microelectronic processing and is usually attributed to classical Fickian diffusion of the acid catalyst. Previous studies have inferred diffusion coefficients from lithographic performance (1). This method is valuable for providing workable engineering parameters, but does not provide much insight into the actual nature of the transport process. The goal of our work is to better understand the transport phenomena that results in image blur. As such, we have tried to design experiments that would allow direct measurement of diffusion coefficients without the many complicating factors inherent in a complete lithographic process.

Several direct measurement techniques were tried unsuccessfully before we arrived at our current method. Our previous attempts were based on capacitance measurements, diffraction grating analysis, and atomic force microscope measurements. Our present technique for measuring acid diffusion is based on spectroscopy, either IR or fluorescence, and requires generation of trilayer polymer film stacks or "sandwiches". The film stack consists of an acid feeder layer, an intermediate layer and a detector layer. The feeder layer contains a photoacid generator (PAG) which generates acid upon ultraviolet exposure. After exposure acid begins diffusing into the intermediate layer. Arrival of acid at the detector layer can be monitored spectroscopically and the diffusion time required to traverse through the intermediate layer can be recorded. The analyzed intermediate layer can be any acid inert polymer such as poly(ethylmethacrylate) (PEMA) or poly(4-hydroxystrene) (PHS). The choice of detector layer depends upon which spectroscopic method is to be employed. For the fluorescence method, the detector layer is a polymer with an acridine based, covalently bonded fluorophore. For the IR method the detector layer is poly(t-butyloxycarbonyloxystyrene) (tBOC) which has an easily monitored acid labile protecting group. Results presented here are from the IR based method; results from the fluorescence method will be presented at a later date.

Experimental

Materials. The tBOC polymer used as detector layer in this study was prepared by free radical polymerization of t-butyloxycarbonyloxystyrene monomer from Hoechst Chemical Co. PEMA, PMMA and PHS were used as intermediate layers in this study. PEMA was obtained from Dupont and used as received. PMMA was prepared by free radical polymerization of methylmethacrylate monomer from Aldrich Chemical Co. PHS was synthesized in our laboratory from p-acetoxystyrene monomer supplied by Triquest. Feeder layer polymers used in this study were poly(4-methoxystyrene) (PMOS) and poly(methylmethacrylate) (PMMA). PMOS was synthesized from PHS, methyl iodide and base. PMMA was prepared as previously mentioned. The photoacid generators used were bis(p-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (PAG #1) and bis(p-*tert*-butylphenyl)iodonium perfluorobutanesulfonate (PAG #2) both from Midori Kagaku, Co. The casting solvent for PHS was ethanol. The casting solvent for tBOC was either toluene or propyl glycol methyl ether acetate (PGMEA) depending on sample preparation method employed. All other polymers were cast from PGMEA. Solvents were purchased from Aldrich and used as received.

Apparatus. A Nicolet Magna 550 FT-IR with an attached liquid nitrogen cooled MCT/B external IR detector from Axiom Analytical was used to collect sample spectra. A nitrogen purged sample chamber attached to a temperature controlled hotplate allowed sample spectra to be collected at elevated temperatures.

Sample Preparation. The trilayer stacks necessary for this experiment were made directly by sequential spin casting when casting solvents could be matched such that each layer would be insoluble in the subsequent layer's casting solvent. Often this requirement could not be met and another approach was required.

The other option available for stack creation was a float process. This method required spin casting each layer on separate substrates, then floating the polymer films onto the surface of water from glass substrates. The floating films were then picked up on a sample substrate containing the underlying film layer(s). After being picked up samples were then dried by heating and/or vacuum desiccation. This method is, of course, limited to polymers that release from their substrate and maintain film integrity during floating.

The sample substrate is a double-polished silicon wafer with gold coating on one side. The gold is necessary to reflect the interrogating IR beam back to the detector while the sample is sitting on the hotplate. This double pass technique eliminates the complexities of standing waves and baseline oscillations. The gold coating was deposited by thermal evaporation and is approximately 100nm thick.

Results and Discussion

Initial work in this study was with PHS as the analyzed polymer layer. PHS is of particular interest because several commercial photoresist formulations are PHS based. Transport properties measured in PHS would be expected to correspond fairly closely to transport properties of actual photoresist systems. But, attempts to measure acid diffusion coefficients in PHS at temperatures ranging from 70°C to 110°C were unsuccessful. Film stacks with PHS layers as thin as 135nm were monitored for up to three days without acid arrival being detected. Figure 1 is a detector layer response curve for a film stack with a PHS thickness of 600nm monitored at 100°C for a day. The response curve was corrected to account for the background rate of uncatalyzed thermolysis observed in tBOC at 100°C. The sample stack was prepared by direct sequential spin casting.

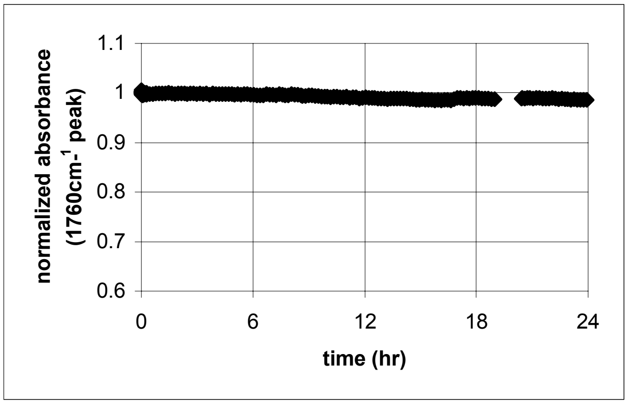

Figure 1. Corrected detector layer response for PHS film stack, T=100°C. tBOC (435nm) / PHS layer (600nm) / PMMA & 10wt% PAG #1 (220nm). Exposure Dose: 40mJ/cm^2

Because line-width spread is a widely observed phenomenon in microlithography, we found the results of our PHS study confusing. Typical line-width spread observed in a manufacturing process is on the order of 30nm to 40nm. This spread occurs during a time period of only a few minutes at elevated temperatures. The apparent diffusion rates we observed could not account for any significant fraction of this spread.

With such unexpected results it was necessary to validate our experimental method by finding an intermediate layer through which diffusion could positively be seen and diffusion coefficients actually measured. It is well known that due to enhanced segmental motion, diffusion in rubbery polymers is usually much faster than diffusion in glassy polymers (2). With this in mind, a polymer with a glass transition temperature (Tg) between 50ºC and 90ºC was found. A Tg in this region allows the polymer to be spin cast to produce a glassy film at room temperature, then transitioned into a rubbery state during the experiment at easily achievable temperatures. The chosen polymer also had to be able to withstand our floating method of sample preparation. The polymer finally chosen was PEMA (Tg = 68ºC). Figure 2 shows observed detector layer response curves for two PEMA film stacks monitored at 90ºC. Each stack was prepared by the float method and had an intermediate layer thickness of 435nm. Two sample runs are shown to demonstrate the repeatability of this method. The response curves shows an acid transit time (τ_{diff}) of 615 seconds.

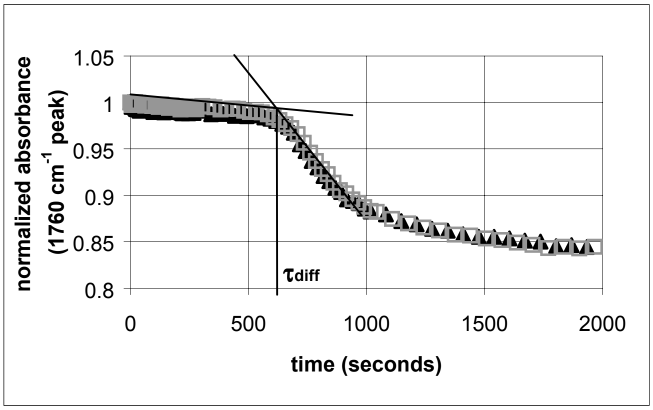

Figure 2. Detector layer response for PEMA stack, T=90ºC.
tBOC (360nm) / PEMA (435nm) / PMOS & 5wt% PAG #2 (260nm) Exposure Dose: 40mJ/cm^2

Once a polymer was found that had an observable diffusion rate, several interesting aspects of the transport process could be investigated. Figure 3 shows that at 90ºC transit time through the PEMA layer scales with the square of the layer thickness. This behavior is exactly that predicted by the classical Fickian diffusion model. Thus, we have observed that above the polymer's Tg acid diffusion occurs by a Fickian-type process. The diffusion coefficient estimated by this method was 3x10^{-4} μm^2/s.

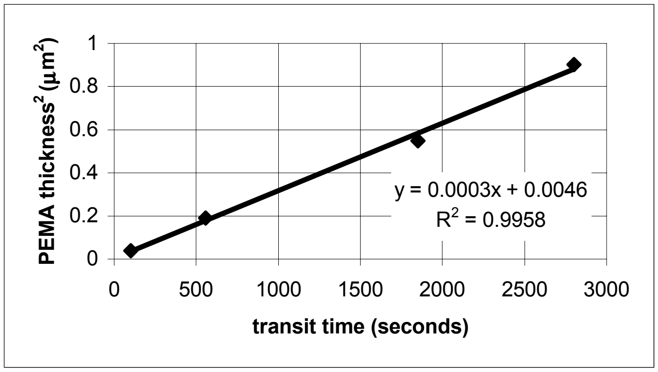

Figure 3. PEMA thickness^2 versus time, T=90ºC. (Classical Fickian behavior)

The effect of temperature on transport behavior was also investigated. Identical PEMA samples were run at temperatures ranging from 65ºC to 95ºC. Transit times were recorded and plotted as a function of temperature in Figure 4. Not unexpectedly, transit time is highly dependent on temperature. The acid transit time increases sharply during the transition from rubber to glass. Very similar results were obtained using PMMA as the intermediate layer. PMMA results were nearly identical to PEMA results, but shifted to a higher temperature range because PMMA's Tg is approximately 110ºC.

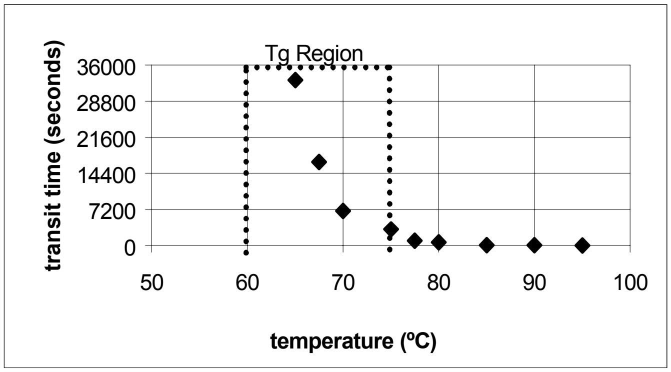

Figure 4. Temperature dependence of transit time around Tg region with a constant PEMA thickness of 150nm.

Figure 4 also provides insight into why diffusion through PHS layers was never observed. PHS has a Tg around a 180ºC; PHS experiments were thus ran at temperatures about a hundred degrees lower than the Tg. Once a rubbery polymer begins the transition to a glassy state, acid transit time begins to increase rapidly. At the temperatures the PHS experiments were ran, the transit time through even just a few hundred nanometers of PHS would likely be something on the order of several weeks, if not months. Currently, experiments near PHS's Tg are not possible because the tBOC detector layer rapidly decomposes at such high temperatures. An effort is currently underway to find a high temperature detector layer to test PHS.

Conclusions

Results from these experiments clearly show that transport properties in thin polymer films are highly dependent on the relation between glass transition temperature and the film temperature. This is to be expected because the transition from glassy state to rubbery state is a phase transition.

It is also clear from these experiments that at typical resist processing temperatures, which are usually well below the resist's Tg, the Fickian acid diffusion coefficient would be extremely small. So small, in fact, that it could not possibly account for observed image blur. The acid transport phenomena that causes image blur proceeds at a much faster rate than predicted by our estimated diffusion coefficients and a classical Fickian model. Either our estimates are several orders of magnitude off from the true diffusion coefficient values, or some other physical model must be used to explain blurring. A model that takes into account the effect of chemical reactions occurring in real photoresist systems is needed to properly explain observed line-width spread. One possible physical model to explain the transport mechanisms in real photoresists is a reaction front propagation model. In this model, as acid catalyst diffuses into unexposed regions, a chemical reaction provides some local enhancement to the transport rate. Local enhancement could be in the form of temporary excess free volume created as gaseous products from deprotection reactions escape the film, or film plasticization due to the same products. Since all the enhancements are transient phenomena lasting only a short time, there is only a small zone at the interface between reacted regions and unreacted regions where the enhancements are active. Behind the reaction zone the reacted region quickly loses its enhanced transport properties as excess free volume collapses or gaseous products escape the film. Acid molecules diffusing out of the reaction zone and into the previously reacted region become trapped in a slow diffusion region and are no longer available to support the front. Acid concentration in the reaction zone quickly declines as the front propagates into the unexposed regions. This model predicts a self-limiting transport process with little concentration dependence. Experimental work is currently being done to verify this model.

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