

Resist Performance Using Spectroscopic Ellipsometry

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Abstract — The technique of spectroscopic ellipsometry was employed to study the effects of residual solvents in chemically amplified photoresists on the dissolution characteristics and optical constants of the spin-cast film. Ellipsometric measurements were made for resist films with no bake, with soft bakes, and with both soft bakes and post-exposure bakes, at various baking temperatures. Exposures of these films were performed using a KrF excimer laser (248 nm) with a beam splitter lens element to increase the exposure area. To increase the accuracy of the experimental data, measurements were made at three different angles over a sampling wavelength range of 200 nm to 800 nm. Resist thickness and optical parameters (n and k) were extracted by fitting the experimental data to a theoretical model.

I. INTRODUCTION

The performance of a photoresist can be characterized by the dissolution rate as a function of exposure. Traditionally, the dissolution rate of the polymer film can only be determined experimentally by measuring the weight or thickness loss as a function of the time in which the resist is submerged in a solvent [1]. Such an approach is complicated by the presence of laterally distributed solvents in the resist, where excess solvent concentration constitutes higher dissolution rate and lower thermal dimensional stability [2, 3]. Since solvent evaporation is higher at the top of the resist film than at the bottom, it can be inferred that the dissolution kinetics of the resist polymer is highest at the top of the coated film and the different development rates could lead to process concerns such as variations in CD measurements and glass transition temperature (T_g). This project employed the technique of spectroscopic ellipsometry to determine such effects for a Poly(t-Boc) Styrene chemically amplified photoresist at various baking intervals. The residual solvent concentration is thus controlled by the magnitude of these baking intervals.

IA. Variable Angle Spectroscopic Ellipsometry

Ellipsometry is a non-destructive optical technique used to obtain accurate and reliable measurements of thin films. As the linearly polarized light reflects off the surface of a sample, it becomes elliptically polarized. The instrument measures the phase change of the reflected light, or the shape of the elliptically polarized light, relative to the incident linearly polarized light. Ellipsometry thus measures the ratio of the Fresnel reflection coefficients for in-plane (R_p) to the out-of-plane polarized light (R_s), as shown by the following equation:

$$\frac{R_p}{R_s} = \tan(\Psi) \exp^{j\Delta}$$

where changes in Δ (delta) and Ψ (psi) relate to the relative phase and amplitude of the reflected light, respectively.

Unlike traditional ellipsometry which measures at only one angle and wavelength, variable angle spectroscopic ellipsometry (VASE), as its name implies, measures at multiple angles over a spectrum of wavelengths (Figure 1). This is particularly advantageous since reflected light behaves differently at various wavelengths and angles of incidence. Furthermore, since the best combination of wavelength and angle depends on the sample structure, VASE can measure a wide range of materials [4].

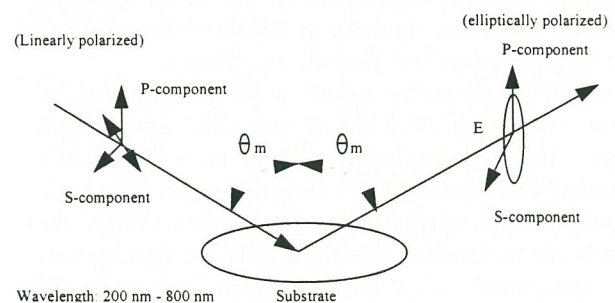


Figure 1: Physical layout of a variable angle spectroscopic ellipsometer.

IB. Interferometry

Interferometry is an effective tool for determining resist development parameters. This technique is based on the principle that when two monochromatic (or nearly monochromatic) light is reflected off two parallel surfaces, interference between the reflected beams will produce an amplitude modulation [5]. The modulation produced is dependent on the phase difference of the reflected beams; that is, beams from the resist-developer interface and the resist-substrate interface. The modulation of the reflected beam is dependent on this phase difference, which, in return, is dependent on the thickness of the photoresist. Thus, as the resist develops, the modulation weakens progressively until all the resist is developed away.

II. EXPERIMENTAL

The resist used in this study was a Poly(t-Boc) Styrene chemically amplified resist with triphenylsulfonium hexafluoroantimonate as the photo acid generator (Shipley UVIII). Refractive index measurements were made after the soft bake, or the post-apply bake (PAB), and again after flood exposure with 248 nm radiation followed by the post apply bake. In addition, a reference sample with no bake was also measured. Each baking intervals had a nominal baking temperature of 130 °C, with 15 °C deviations, as illustrated by Table 1 below.

Baking interval	Temperature(s) in °C
PAB only	115, 130, 145
PAB, Exposure, and PEB	115, 130, 145
No Bake	NA

Table 1: Baking intervals and temperatures

Flood exposures were performed with a KrF excimer laser with a nominal dose of 50 mJ/cm² at an operating frequency of 50 Hz. In order to maximize the exposure field, a beam splitter lens element was utilized.

For the interferometry set-up, a HeNe laser with an output wavelength of 6,328 Å was used as the light source. This light was directed to the photodetector via a bifurcated fiber optic cable. Once the wafer and cable assembly was submerged in the developer solution, the resist began to develop. The signal from the detector was then transferred to a plotter which displayed the amplitude modulation as the resist develops.

III. RESULTS AND DISCUSSION

The effects of baking had a significant impact on the refractive index (n) and the extinction coefficient (k) of the resist. In particular, the refractive index appeared to baseline between 1.5 and 1.55 for increasing wavelength when baked as oppose to a steady decreasing trend with no bake, as shown in Figure 2. However, the effects of baking temperatures did not seem to effect the refractive index much as variations between these runs were minimal. The refractive index first appeared to decrease with increasing baking temperature, but then the trend stopped, suggesting that all the solvents had been driven out of the resist and thus the film became densified, preventing further changes in "n."

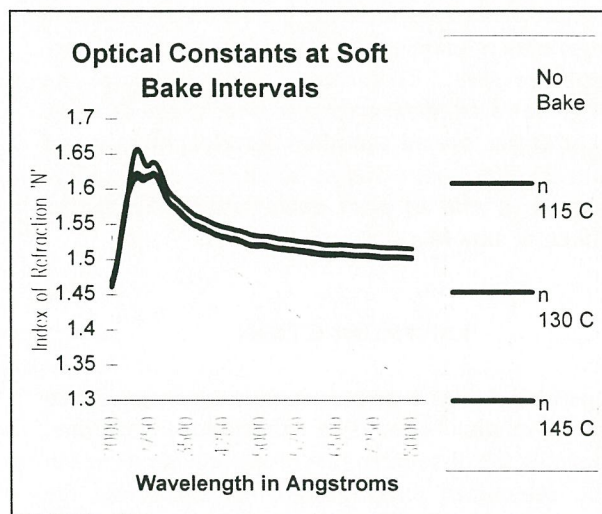


Figure 2: Refractive index measurements after the post-apply bake.

The effects of baking also had a dramatic effect on the extinction coefficient of the resist (Figure 3). With no bake, there was a strong absorption ($k = 0.35$) near 280 nm, a region relatively close to the exposing wavelength. However, all three soft bake temperatures suppressed the absorption signature to a value close to 0.05, a 86% reduction in absorption. This characteristic is highly desirable since that the polymer should be as transparent as possible at the exposing (or near) wavelength in order to transfer the maximum number of photons to the photo acid generator component of the resist, which is

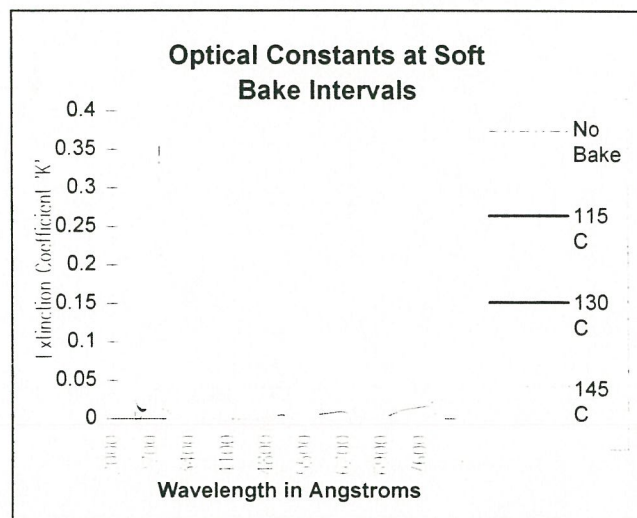


Figure 3: Extinction coefficient measurements after the post-apply bake

responsible for initiating the deprotection process upon exposure.

The additional post-exposure bake following flood exposure revealed a refractive index characteristic very similar to that with only the PAB baking level. Refractive index values also baselined between 1.5 and 1.55 for increasing wavelength. The absorption signature, however, lowered with the additional bake and exposure (Figure 4). A reduction as much as 25% was observed at the measuring wavelength of 220 nm with extra baking. It is also interesting to note that, like the previous plots with only the PAB, differences in baking temperature did not cause variations in both "n" and "k" measurements.

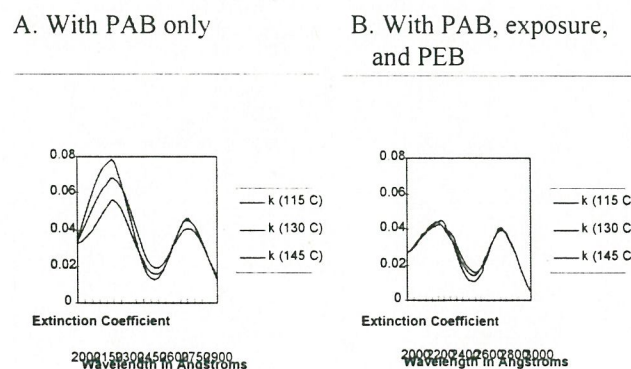


Figure 4: Effects of the additional post-exposure bake on the

The dissolution study was the most difficult part of this project. No amplitude modulation was observed for both exposed and unexposed resists in the interferometric measurements. Numerous attempts were made to overcome this difficulty, but results are still pending. Developers of different normality concentration were also used in the study, but it appears that while the exposed resist developed too rapidly in the developer, the unexposed resist developed much too slowly.

IV. CONCLUSION AND FUTURE WORK

This project demonstrated the effectiveness of variable angle spectroscopic ellipsometry in determining the effects of baking on the performance of a photoresist. By fitting the experimental data to a theoretical model, optical parameters of the resist were able to be extracted. It was learned that while baking had a significant impact on both the refractive index and extinction coefficient parameters of the resist, variations in baking temperatures do not. Without bake, there was a strong absorption signature near 280 nm, a region close to the exposure wavelength of 248 nm. However, with baking, at any interval and any magnitude, the absorption trace was greatly suppressed.

Future work might include investigating alternative ways to measure the development parameters of the resist. Once the dissolution data is obtained, then an empirical model can be derived using the data collected thus far to arrive at an expression that describes the dissolution characteristics of the resist at any given time during development.

V. ACKNOWLEDGMENT

The author would like to thank the following individuals for their contributions to this project: Dr. Bruce Smith, for the technical support and assisting with the ellipsometry measurements; Howard Ashburn of Shipley Company, for providing the process parameters for the UVIII resist; and Dr. Santosh Kurinec, for overseeing the final preparations of this paper.

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