Photoresist Absorbance and Bleaching

Andrew Estroff
Microlithography Materials, Microelectronics Engineering Department, Rochester Institute of Technology

ABSTRACT

The goal of this experiment was to characterize the relationship between a photoresist's absorbance and photosensitivity. Three different photoresists were examined – Shipley System8 (812), a DNQ based g-line resist, OiR620, a DNQ based i-line resist, and ARCH8250, a PHOST based DUV resist. Absorbance vs. wavelength plots were made both pre- and post-exposure for each photoresist to demonstrate the decrease in absorption (bleaching) of the photoresist after it had been exposed. The two non-DUV photoresists both experienced a large decrease, whereas the ARCH8250 DUV photoresist experienced no bleaching after exposure. The A, B, and C parameters were derived from a plot of transmitted radiation signal intensity, and were found to be 0.957um^{-1}, 0.0505 um^{-1}, and 0.0142 cm^{2}/mJ for Shipley System8 and 0.762 um^{-1}, 0.0824 um^{-1}, and 0.0132cm^{2}/mJ for OiR620. Dill's ABC parameters were not calculated for the ARCH8250 DUV photoresist.

Keywords: Photoresist, absorption, transmission, Dill parameters, bleaching.

1. INTRODUCTION

The lithography process is undoubtedly the most heavily used process in semiconductor manufacturing; every level on a chip is defined by the photolithography process. In addition, it is one of the most costly processes, with a modern lithography system (coat track and stepper/scanner) costing in the range of six to twenty million dollars, not taking into account the mask making costs, number of masks needed, nor the chemical costs. Therefore an optimized and well-characterized lithography system is desired so that the manufacturing process is highly robust.

A key component of the lithography system is the photoresist, a medium that allows for the transfer of an image from the mask to the wafer. Hence, it is essential to characterize a photoresist in order to use it efficiently. An important characteristic of a photoresist system is how well it absorbs radiation before and after it is exposed to radiation. This characteristic is described by the Dill absorption parameters: A, B, and C.

2. THEORY

The photoresist system consists of three main components: a photoactive compound (PAC), a base resin, and an organic solvent system. Without the photoactive compound, a film consisting of only the base resin has a relatively high removal rate in an aqueous alkaline solution. However, with the photoactive compound incorporated into the film, the removal rate is greatly reduced. When the photoactive compound is destroyed by incident radiation, the removal rate of the film is drastically increased to levels much higher than those attainable when the photoactive compound was not present in the film.

The ability of a photoresist to absorb this incident radiation influences the resolution and process capabilities of the photoresist. As the photoactive compound is destroyed by the incident radiation, the absorption of the photoresist decreases; this phenomenon is known as bleaching. Both maximum transmission and maximum absorption are highly sought after, and thus there is an optimum resist absorbance value for any photoresist thickness. The higher the transmission of the resist, the easier it is for the incident radiation to reach the bottom of the film. The greater the absorption of the resist, the lower the exposure dose required to destroy the PAC, making the resist more efficient, allowing for higher throughput.

Bleaching can be described by using the Dill absorption parameters A, B, and C:

$$A = (1/d)*\ln[T(f)/T(0)] \quad [um^{-1}]$$

Equation 1: Calculation of Dill absorption parameter A

$$B = -(1/d)*\ln[T(f)] \quad [um^{-1}]$$

Equation 2: Calculation of Dill absorption parameter B

$$C = [(A+B)/(A*I_o*T(0)*(1-T(0)))]*(dT(0)/dt)|_{t=0} \quad [cm^2/mJ]$$

Equation 3: Calculation of Dill absorption parameter C

In equations 1-3, d is the coating thickness, T(0) is the transmittance of the film prior to exposure, T(f) is the transmittance of the film after bleaching or a high exposure dose, $(dT(0)/dt)|_{t=0}$ is the initial change in transmittance, and I_o is the light intensity at the top of the film. The A parameter is the exposure dependent term, thus providing information on light absorption due to the photoactive compound. The B parameter is the exposure independent term and provides information on the absorption of the base resin of the photoresist. The C parameter yields information the bleaching rate of the photoresist during exposure; C relates directly to sensitivity in novolac based resists. It is desired for the B parameter to be a small value in order to maximize resist transmission.

3. EXPERIMENTAL PROCEDURES

3.1 Spectrophotometry Procedure

Three, four-inch square quartz substrates were used for this portion of the experiment. First, the substrates need to be coated with photoresist. To do this, a substrate underwent a dehydration back at 150^{o}C for 90 seconds, followed by an HMDS liquid prime comprised of first placing the substrate in the P6700 spinner, applying a puddle of HMDS, and spinning at 3000RPM for 45 seconds, followed by a bake at 150^{o}C for 3 minutes. After the substrate had cooled, it was put back on the spinner for photoresist apply. A puddle of Shipley System8 (812) resist was placed on the wafer, which was then spun at 3000RPM for 45 seconds, followed by a bake at 100^{o}C for 3 minutes.

Following the photoresist apply step, the substrate was scratched across its diagonal in order to take thickness measurements using a Tencor P-2 profilometer. Two measurements were taken on opposite sides of the substrate.

Next, the Perkin-Elmer Lambda 11 UV-vis spectrophotometer was calibrated for wavelengths varying between 190-800nm using a blank quartz substrate. The autozero program was run with background correction. The substrate was placed in the spectrophotometer with the resist facing the light source, and the transmittance was measured for different wavelengths from 190-800nm. The data was saved as GBS812U1 (**G**roup **B** **S**hipley**812** **U**nexposed **1**) so that it could be collected later. The substrate was then rotated 90^o and transmittance was measured again (GBS812U2).

After the spectrophotometry measurements were taken, the substrate was taken to the GCA6700 436nm g-line stepper for flood exposure. The substrate was placed on top of another glass plate on the reticle stage, the optical column was closed, and the wafer was flood exposed for 50 seconds (300mJ/cm^2). Following the exposure, transmittance measurements were taken again using the spectrophotometer in the same fashion as above, using the same naming convention to save the data.

The data was retrieved at a later date and the absorbance was plotted vs. the wavelength. Transmission is converted to absorbance by equation 4 below:

$$a = (1/thickness)*\ln(T)$$

Equation 4: Converting Transmission (T) to absorbance (a)

This entire procedure was repeated for both the OiR620 and ARCH8250 DUV resists, with the only change in procedure being the type of photoresist applied to the substrate. The ARCH8250 DUV photoresist only had its transmittance measured once, it was not rotated 90^o and measured a second time.

3.2 Actinic Absorption and A, B, C Measurement

Four microscope slides were used for this portion of the experiment. They were first cleaned with IPA to ensure cleanliness. The spinner chuck on the P6700 manual spinner was replaced with a ½" diameter chuck to accommodate the small substrate size. The substrates were coated with HMDS and photoresist following the same procedures used in section 3.1. Two slides were coated with Shipley System8 (812), and the other two were coated with OiR620.

After the resist apply step, a scratch was made across the slide so that a thickness measurement could be made using the Tencor P-2 profilometer. One slide coated with Shipley System8 was measured as was one slide coated with OiR620.

A strip chart recorder in combination with a UV photodetector was then setup to measure the radiation transmitted through the resist coated microscope slide from the GCA6700 g-line stepper. The photodetector was placed on a glass reticle on the reticle stage of the stepper. A resist coated microscope slide that was not to be used for data collection was placed on the photodetector, and the shutter on the stepper was opened to begin exposure of the photoresist. The plotter was calibrated so that the entire transmitted radiation signal intensity curve could be plotted until there was no change in the response calibration speed = 12.7 seconds/inch). In addition, an intensity measurement was made (Io).

Following calibration, a microscope slide coated with Shipley System8 resist was placed on the photodetector, the strip recorder was started, and the stepper shutter was opened to begin exposure. The shutter was closed when there was no change in the response. After the exposure of the photoresist, a blank microscope slide was placed on the photodetector, the stepper shutter was opened, and the strip chart recorder turned on to measure the transmission of a blank slide. The initial intensity signal was labeled S(0), the final intensity S(f), and the intensity through a blank slide S(s). This was repeated for a microscope slide coated with OiR620.

From these plots, S(s), S(0), S(f), and the slope of the linear portion of the plot was used to calculate the A, B, and C parameters.

4. RESULTS AND ANALYSIS

4.1 Spectrophotometry Results

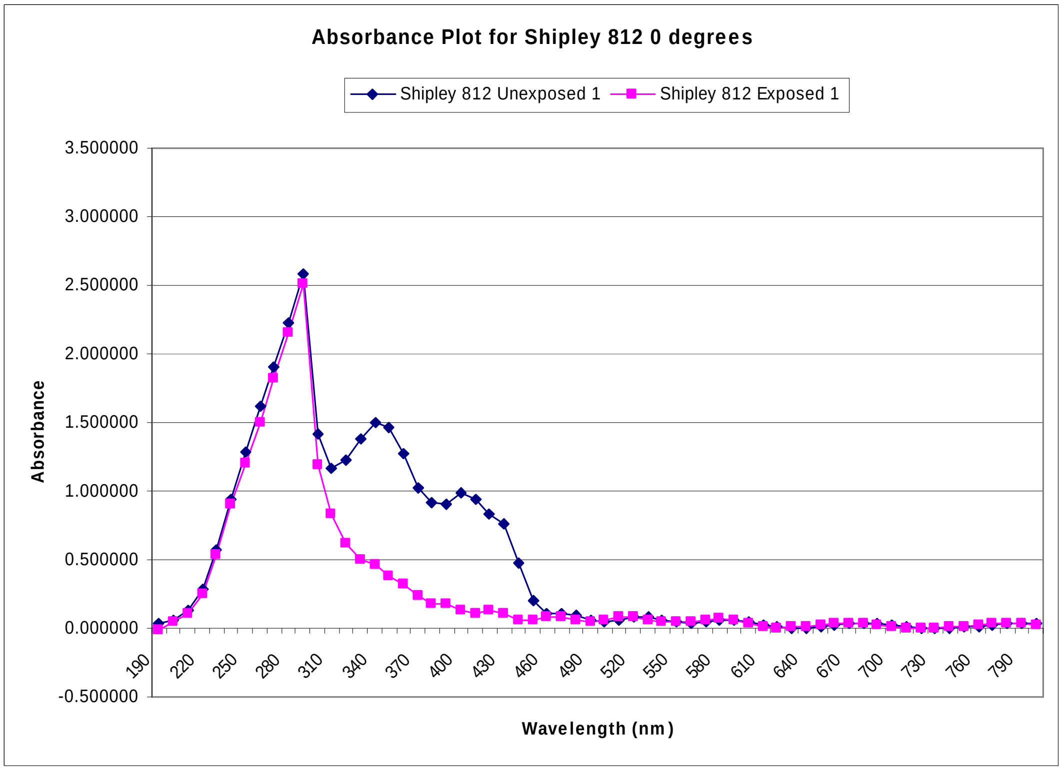

Figure 1: Plot of Absorbance vs. Wavelength for Shipley 812, Rotated 0 degrees

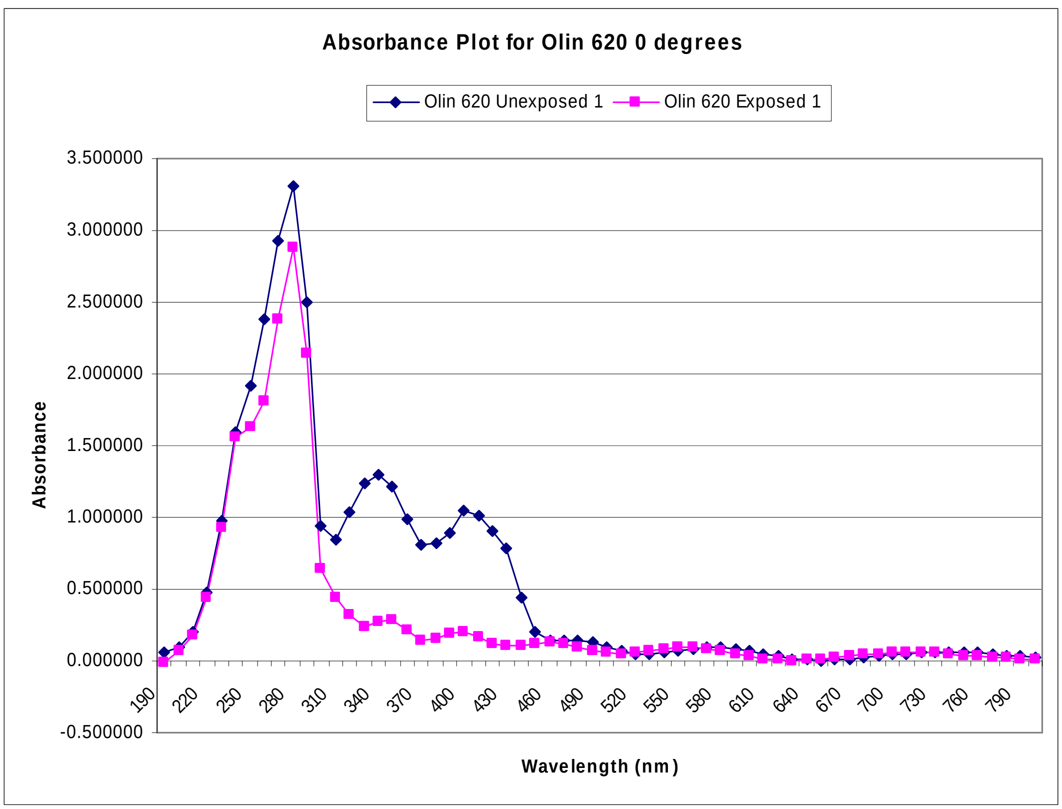

Figure 2: Plot of Absorbance vs. Wavelength for OiR620, rotated 0 degrees

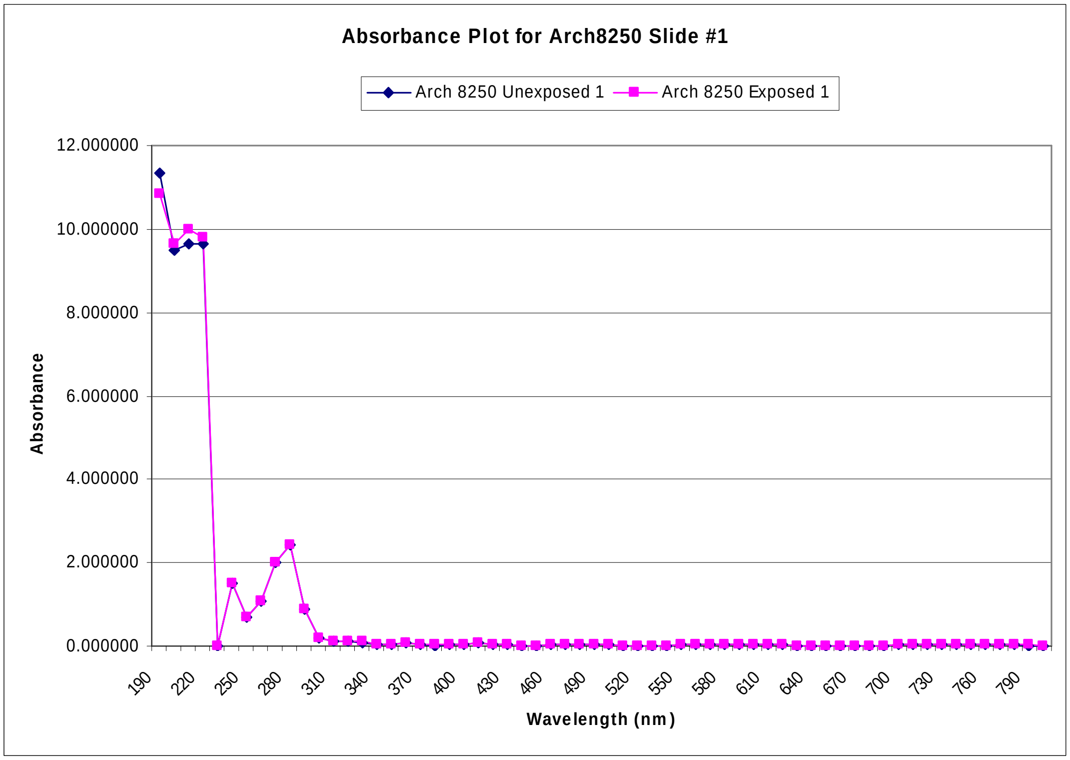

Figure 3: Plot of Absorbance vs. Wavelength for ARCH8250 DUV resist

Appendix A contains the full size plots of figures 1-3 so that the data on the plot can be read more easily. Appendix A also contains the plots after the substrate was rotated 90 degrees, however, there is virtually no change from the non-rotated samples, so the plots were not included in this section.

4.2 Analysis of Spectrophotometry Results

When comparing the two non-DUV resists (figures 3A, 3B, 4A, and 4B), there is no immediate difference between the absorbance vs. wavelength plots. Intuitively, this should not be surprising. Both Shipley System8 (812) and OiR620 are DNQ-novolac based photoresists, thus their absorbance before and after exposure shouldn't differ from one another greatly. Prior to exposure, both resists have absorbance peaks around the g- and i-lines (436 and 365nm respectively). This plot demonstrates that both photoresists absorb well at these two wavelengths prior to exposure. Both of the resists are highly absorbent at 300nm and below, which is why they are unsuitable for DUV exposure.

After being exposed, however, there is a subtle change in the two plots. Shipley System8 is a photoresist optimized for g-line exposure, and the absorbance at the g-line peak after exposure is quite low, showing that the B parameter, the exposure independent term, representing the novolac base resin, does not absorb much at 436nm. There is high contrast between the pre- and post-exposure absorbance peaks at 436nm, demonstrating the bleaching properties of the resist. OiR620, which is a i-line optimized resist, has an even lower absorbance value after exposure at the i-line wavelength than does the Shipley System8; the Shipley System8 resist has a slightly higher absorbance at i-line after exposure than OiR620, but still demonstrates good contrast between pre- and post-exposure. It appears as though the base resin for the OiR620 has been finely-tuned to absorb less i-line radiation, thus providing better contrast. Figure 2 also shows how OiR620 bleaches after exposure.

The DUV resist, ARCH8250, is designed for exposure at a wavelength of 248nm. ARCH8250 DUV resist does not bleach after exposure. The pre- and post-exposure plots follow one another almost identically. Figure 3 shows that it absorbs well at approximately 248nm.

4.3 Actinic absorption and ABC measurement results

	Shipley System8	OiR620
d [um]	1.10	0.7771
Slope	1.3	1.3
S(0) [AU]	3.7	5.8
S(f) [AU]	10.6	10.5
S(s) [AU]	11.2	11.2
T(0)	0.330	0.519
T(f)	0.946	0.938
dT/dt [sec^{-1}]	0.0182	0.0182
A [um^{-1}]	0.957	0.762
B [um^{-1}]	0.0505	0.0824
C [cm^2/mJ]	0.0142	0.0132

Table 1: Results from the transmitted radiation signal intensity plot

4.4 Analysis of actinic absorption and ABC measurement results

Shown in Appendix B are the transmitted radiation signal plots for Shipley System8 and OiR620 resists. S(0) for the Olin620 is a higher value than S(0) for the Shipley System8 resist, thus denoting lesser absorption/greater transparency of the OiR620 resist. This is represented by the OiR620's smaller A value. However, it should be noted that Beer's law states that transmittance of unexposed photoresist decreases logarithmically with thickness. Since the OiR620 is thinner than the Shipley System8, it should exhibit better transmission.

The rate at which the absorption changes from A+B prior to exposure to only B after exposure (parameter C) is very similar for both resists. The transmitted radiation signal plots for both resists have the same slope (even if some error is taken into account, the slope does not differ greatly between the two resists).

The exposure independent term, B, is slightly higher for the OiR620 photoresist than for the Shipley System8; OiR620 has a lower S(f) value, representing a lower transmission after bleaching has occurred. At 365nm, the absorbance of OiR620 is less than that of Shipley System8, but the absorbance of OiR620 is greater at 436nm than the absorbance of Shipley System8 at that same wavelength. Again, this highlights the fine tuning of the base resins of OiR620 for exposure at 365nm, and Shipley System8 for exposure at 436nm.

Since A, B, and C are wavelength dependent, it is logical that the absorbance might be higher or lower for a given resist before or after exposure at different wavelengths.

5. CONCLUSION

This experiment examined the relationship between a photoresist's absorbance and photosensitivity. From table 1 it can be concluded that the higher absorbance a resist exhibits, the faster it will bleach, exhibiting greater sensitivity. However, there is a trade off between transmission and absorption. If the resist absorbs too much, the bottom of the film will not get exposed.

There were a few subtle differences between the two DNQ-novolac, non-DUV photoresists, but besides some enhancements to increase their performance at a specific wavelength, they performed very similarly. They both exhibited high contrast at g- and i-line, with the g- and i-line resist each showing a slightly better contrast at the wavelength they were respectively tuned to perform optimally at. The major discrepancy from the experiment was between the ARCH8250 DUV resist and the two non-DUV resists. The ARCH8250 DUV resist does not bleach upon exposure.

REFERENCES

1. F.H. Dill, W. P. Hornberger, P.S. Hague, J.M. Shaw, "Characterization of Positive Photoresist", IEEE Transactions on Electron Devices, Vol. ED-22, No. 7, July 1975
2. Sheets and Smith, Microlithography: Science and Technology, Marcel Dekker, Inc., 1998, printing 4.
3. http://willson.cm.utexas.edu/Research/Sub_Files/Photomask_Lithography/Files/SPIEPaperFinal.PDF B.M. Rathsack, C.E. Tabery, S.A. Scheer, "Optical Lithography Simulation and Photoresist Optimization for Photomask Fabrication"
4. http://appserver.microe.rit.edu/classes/emcr666_676/absorptivity/ResistAbsorbanceLab.pdf "Photoresist Absorbance and Bleaching Laboratory" handout, Microelectronics Dept., Rochester Institute of Technology.