Photoresist Absorbance and Bleaching Laboratory

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1. OBJECTIVE

The objective of this experiment is to understand and characterize the relationship between absorbance and photosensitivity for photoresist materials.

2. INTRODUCTION

Exposure of photoresist involves the absorption of radiation and subsequent photochemical change, generally resulting in a modification of dissolution properties. The absorption characteristics of a photoresist will largely influence its resolution and process capabilities. Resists based only on exponential attenuation of radiation (i.e. with no mechanism for photo-bleaching or chemical amplification) can be limited by a maximum allowable contrast, sidewall angle, and ultimate resolution. This is because of the inherent absorption trade-off required when imaging into a resist film. Both maximum transmission (to reach to the bottom of the resist) and maximum absorption (to achieve highest sensitivity) are desired. There is therefore an optimum resist absorbance value for any resist thickness.

The dynamic absorption that exists for the sensitizer for novolac resists occurs as exposure leads to a more transparent photoproduct. This bleaching phenomenon can be described in terms of the Dill absorption parameters A, B, and C [see Optical Lithography - F.H. Dill (1975)]. The A parameter describes the exposure dependent absorption of the resist, the B parameter is the exposure independent absorption, and C describes the rate of absorption change, or bleaching rate. For novolac resists, the C parameter conveniently relates directly to resist sensitivity since photo bleaching corresponds to the conversion of the photoactive compound (PAC) to the photoproduct. The choice for a specific sensitizer compound for mid-UV lithography needs to include evaluation of the unique A, B, and C parameters at the wavelength of exposure. It is generally desirable to have a low exposure independent absorption (B parameter) to achieve maximum exposure efficiency to the bottom of a resist layer.

Chemical amplification is another avenue that exists to improve the absorption characteristics of a resist. With quantum efficiencies that are several orders of magnitude higher than what can be achieved for direct photo-modified resists, only a small amount of photon absorption is needed. The down side of such high transparency for resist materials is the increased opportunity for substrate reflection to degrade performance. These effects can be manifested as line width variation over reflective steps (notching) and sidewall standing wave. The reduction of these standing waves is crucial in order to retain CD control. This can be dealt with in either resist exposure or process stages and is ordinarily addressed in both. To reduce standing waves effects during exposure, the reflected contribution must be controlled. This can be accomplished by incorporating a dye into the resist formulation. Dyes such as coumarin or curcumin compounds have been used as additives to novolac resists and are very effective at reducing the reflected exposure contribution in a resist layer at g-line and i-line wavelengths. By adding a dye, the exposure independent absorption is increased. The result will be a decrease in reflection effects and standing wave but also a decrease in the amount of energy transferred toward the bottom of the resist. This will result in a decrease in sidewall angle, resist contrast and sensitivity. Dyed resist for i-line use is therefore usually limited to highly reflective, non- critical layers.

3. MEASUREMENT OF RESIST ABSORPTION

This lab will involve the measurement of resist absorption. Two methods will be utilized:

3.1) Spectrophotometric measurement of absorption through wavelength.
3.2) An actinic measurement of absorption and bleaching at lithography wavelengths.

3.1 Spectrophotometry procedure

A Perkin Elmer UV/VIS spectrophotometer will be used to measure the unexposed and exposed absorption of photoresist. Before performing the lab, turn on the Perkin Elmer ~30 minutes prior to running anything (green switch near the back). The computer should already be on (if it is not, the computer needs to be turned on before the Perkin Elmer).

1. Obtain a 4" quartz fused silica mask substrate.
2. Clean (with isopropanol) and dehydrate bake the substrate at 100°C for 5 minutes and HMDS liquid prime @3000RPM, followed by a bake at 100° for 1 min.
    a. Placing the silica wafer directly on a hot-plate will send it into thermal shock and break it. To avoid this, slowly slide it on to the hot-plate from the side.
3. Coat photoresist at 3000 RPM, and bake at 100° for 3 min. Measure thickness via profilometry, or Nanospec a silicon wafer coated with identical settings.
    a. Remember to place the coated wafer in an opaque container when traveling outside the yellow light environment.
4. Use the PE Lambda 11 UV-VIS spectrometer to measure transmittance of film from 200- 800 nm. Follow the procedures given below to obtain ASCII data for plotting. Calculate and plot the absorbance of the photoresist in units of μm-1.
    a. Once the tool has initialized, open PECSS (shorcut on the desktop).
    b. Press Shift-F10 to open the menu, then once the menu shows up at the bottom of the screen, press Enter for Scan.
    c. Input the desired filename, turn on autosave, and set to measure transmission. When finished, press enter until some options appear at the bottom (Y)es (N)o (A)utocalibrate.
    d. Run (A) first to record the background spectrum with no substrate. Then run (Y)es for the each sample. The data should automatically be saved as whatever you named the file.
    e. Hit the escape key and type STOP to exit.
    f. Data files need to be convert to ".dif" files. These are ascii delimited text.
5. Flood expose resist sample using GCA6700 stepper at the reticle stage using a dose of 300 mJ/cm^2.
6. Repeat transmission measurements from 200-800nm and collect data.
7. Plot absorbance for both exposure cases as well as bleaching effects.
    a. Use the Beer-Lambert law $T = e^{-\alpha t}$ to derive absorption from the transmission data, where t is the film thickness, and α is the absorption coefficient.

3.2 Actinic absorption and *A, B, C* measurement

Measurement of resist absorption parameters can be carried out based on the Dill method [see Characterization of Positive Photoresist - F.H. Dill, W.P.Hornberger, P.S. Hauge, J.M. Shaw (1975)]. These values can then be used as inputs in the simulation programs. In this experiment, glass microscope slides will be used as substrates for the resist film. A photoresist film coated on a transparent substrate is exposed to radiation from a lithography exposure tool (such as the GCA g-line stepper). The radiation transmitted through the resist-substrate is measured as a function of time. The absorption parameters of the resist can be calculated from the dynamic transmission of the film. Parameter *A* gives information on light absorption due to the PAC. Parameter *B* gives information on the base absorption of the resist excluding the PAC. Parameter *C* gives information on the bleaching rate of the photoresist during exposure. The following procedure will be used.

8. Using a multimeter, an amplifier, a database application, an extension cord, an electrical outlet splitter (or another extension cord), and a UV photo-detector; set up an experimental measurement apparatus to collect the radiation transmitted through a resist coated microscope slide. The GCA 6700 stepper will be used as the g-line radiation source, and the i-line hood will be used as the i-line radiation source.
    a. Plug in the amplifier ahead of time; the gain increases as the device warms.
    b. Use the photo-detector to measure the irradiance of the tool.
    c. Attach the photodiode into the back of the amplifier, and mount the sample above it in the optical column if appropriate (you will collect data without a substrate, with an uncoated substrate, and with a coated substrate).
    d. Reset the GCA's aperture blades to home position with the command RMS followed by 'AP'R' and then exit RMS with ~
    e. Play with the range and sensitivity so that the output voltage does not peg when the shutter is open.
        i. Range C, Sensitivity Factor $x10^{-6}$ has worked in the past.
        ii. The amplifier should be in D.C. mode.
        iii. Keep an eye on the output to ensure the gain has not drifted over time.
            1. If this occurs and the range or sensitivity factor must be changed, remember to take another set of measurements for calibration.
            2. Even if it doesn't peg, the amplification will drift, so take calibration measurements around the same time as when the slides get exposed.
    f. Using two banana plugs, connect the amplifier's ground and 1000mV Recorder Output ports (found on the backside) into the 1000Vmax and ground inputs on the front of the multimeter.
    g. Connect the multimeter to the computer with the serial cable.

h. Turn on the multimeter
    i. The display should briefly read RS-232
        1. If not: Shift, menu, “right” to I/O menu, “down” to GPIB addr, “right” to Interface, “down”, “right” until RS-232, Enter
    ii. If the multimeter does not respond to chances in irradiance, cycle the power on the multimeter (this will happen if the photodiode is disconnected and then reconnected).
i. Open Excel Intulink
j. Click on the first button in the Intulink toolbar (Connect to multimeter)
    i. Identify instruments
        1. Parity: Even
        2. Size 7
        3. Baud Rate 9600
        4. Handshake DTR/DSR
        5. O.K.
    ii. Click on the multimeter, Connect, Close.
k. Click the third button on the Intulink toolbar (Set up multimeter)
    i. D.C. voltage
    ii. Auto range
    iii. Resolution 4
    iv. O.K.
l. Click the fifth button on the Intulink toolbar (Setup/run logging worksheet)
    i. Set desired values for sampling frequency and duration.
        1. 0.2 is the minimum permitted sampling interval.
    ii. O.K. (Don’t click just yet)
        1. Once the O.K. button is pressed, a new worksheet is created and data collection begins.
m. Stop, pause, and play in the toolbar can be used, but it is best to be prepared prior to pressing O.K.

9. Obtain four microscope slides. Clean (with isopropanol) and dehydrate bake the slides at 100°C for 5 minutes and HMDS liquid prime @3000RPM, followed by a bake at 100° for 1min.
10. Coat photoresist at 3000 RPM, and bake at 100° for 3 min. Measure thickness via profilometry.
11. Click the O.K. button in the Setup/run logging worksheet window in Excel to begin data collection. Allow several seconds of data collection to pass before opening the shutter and exposing the photoresist to get a “dark voltage” calibration measurement.
    a. The curve traced in Excel represents the transmitted radiation signal intensity. Continue to expose until there is no longer any change in response; this is the measurement of the final intensity signal.
    b. Drag the control slider titled “Max Points on Strip Chart” all the way to the right to view the plot in its entirety.
12. Measure the transmission of a blank glass slide. This is a measurement of the signal through the

substrate.

13. Measure the transmission with no slide. This is a measurement of the signal with transmission equal to 1. Note this can be used to estimate opening (rise time) and closing delay for the shutter.
14. Calculate and label the y axis of the plot for voltage signal, irradiance, transmission, and absorption from your collected data.
15. Derive *A*, *B*, and *C*. Compare results with those from the spectrophotometric measurement.
16. Repeat steps 1-15 for assigned resists and radiation sources.
17. Compare results from the two resists and explain differences.
18. Remember to turn off the amplifier to avoid running down the battery.