Determined spectral sensitivity of Kodak Micro Positive Resist 820

Matthew L. Huck
DETERMINING SPECTRAL SENSITIVITY
OF KODAK MICRO POSITIVE RESIST 820

by

Matthew L. Huck

A thesis submitted in partial fulfillment
of the requirements for the degree of
Bachelor of Science in the School of
Photographic Arts and Science in the
College of Graphic Arts and Photography
of the Rochester Institute of Technology

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Date April 15, 1983
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Submitted to the Photographic Science and Instrumentation Division in partial fulfillment of the requirements for the degree of Bachelor of Science in the School of Photographic Arts and Science in the College of Graphic Arts and Photography of the Rochester Institute of Technology

ABSTRACT

The spectral sensitivity of KODAK Micro Positive Resist 820 has been determined for the spectral range of 300nm to 500nm. A xenon-source monochrometer was used in a hard contact exposing system. Sensitivity is defined as the inverse of the exposure (μJ/cm²) needed to produce an image in a photoresist coated plate having walls of 70° normal slope. Low intensity reciprocity law failure has been conclusively shown to exist in this resist with exposure intensities of 100 mw/cm² and below. Guide lines have been drawn up, based on the procedures and results of the experimentation, to assist photoresist users in determining the spectral sensitivity of a photoresist. The feasibility of these procedures has been determined to be positive.
ACKNOWLEDGEMENTS

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DEDICATION

This thesis is dedicated to
my fellow classmates,
whose help, encouragement,
and support, has made the four years
at RIT and this thesis,
a rewarding and satisfying experience.
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I. INTRODUCTION

Photoresist is a non-silver, photo-sensitive material. It is typically sensitive in the deep blue and UV regions of the electromagnetic spectrum. Generally, photoresists are polymers, like a diazo resin, or photo polymerible materials, such as polyvinyl cinamate. Photoresist, simply referred to as resist, is used in the semiconductor industry for the formation of images. These images are relief in nature and, therefore, can be used to protect particular surface areas during the chemical or plasma etching in the semiconductor fabrication process.

The semiconductor chip, which is comprised of a number of different levels throughout the manufacturing process, begins with a schematic drawing of the electrical circuit. Through computer assisted design (CAD) systems, the schematic is broken down into these various levels. Each level has a mask, a piece of glass with an opaque chrome image which defines that level. For an example, see Figure 1.

Resist, in a liquid form, is coated onto a substrate of either a glass plate (for mask production) or a silicon wafer (for the actual device production). The substrate is spun, either before the resist is applied to the substrate (static-spin) or during the placement of the resist onto
the substrate (dynamic-spin), allowing the resist to coat smoothly and evenly across the surface.

Figure 1
A sketch of a typical mask

Silicon wafers are generally used for the fabrication of semiconductors because they provide a surface to work and build upon, and because their electrical properties can be selectively modified. Germanium is another such material, but it is used less frequently than silicon because of its high cost. Both materials lie between the metals (conductors) and non-metals (non-conductors) of the
periodic table. With the correct chemical treatment, these materials act as conductors or non-conductors, hence, semiconductors.

For each level, an exposure is made through a mask to form an image in the resist. This image will have a unique purpose in the production of the chip. For some specific level, as an example, the resist image could be used to prevent the removal of the substrate\(^2\), prevent the deposition of a material, or to form an optically dense mask for a secondary exposure.

As each level is completed, a three dimensional structure is built on top of the wafer. This structure behaves as a matrix of resistors, transistors, capacitors, etc., and this makes the semiconductor function as a circuit.

For a general overview of the semiconductor fabrication process see References 4,5.

Resists are categorized as being either positive or negative, depending on the specific method of image formation. The relief images are formed upon processing, in general, because of a difference in solubility of the resist as a result of an exposure.

In the case of a diazo (positive) photoresist, areas which receive sufficient energy, radiant or thermal, undergo a reaction which causes nitrogen bonds to break apart forming an unstable compound which in the presence of
water, forms indenecarboxylic acid. This results in an area with significantly greater solubility to a basic solution than the areas which did not receive exposure. Exposed areas are then washed away by this solvent while unexposed areas remain.

Conversely, with a negative resist, areas which receive sufficient energy, radiant or thermal, undergo a formation of chemical bonds through a free radical reaction, decreasing its solubility to a particular solvent. Exposed areas become insoluble to this solvent while the remaining areas are washed away by the solvent.

As the amount of actinic energy exposing a positive resist increases, the number of chemical bonds breaking also increases. As a result, if the image which is being exposed were a clear-bar (space), an increase in exposure from the norm would produce a space of greater width than that of a normal exposure. Simply put, for a positive resist, as exposure increases, images of dark-bars decrease in width and images of clear-bars increase in width. The same holds true for negative resist, except, that the image produced from a dark-bar is a space rather than a line of resist as is with positive resists.

For a more rigorous explanation of the workings of positive and negative resists see Reference 3, 7, 8, 9.

A number of parameters must be considered when choosing a photoresist. Among these, adhesion, etch
resistance, resolution, sensitivity, and step coverage must be characterized\textsuperscript{10,11,12}. Of the parameters which directly effect the imaging, sensitivity and resolution are the two most important.

The critical dimensions (CD's), or line widths, of the image which defines the electrical path of the device being manufactured, are extremely important to the electrical properties of that device. If the line width of the electrical path either increases or decreases, the electrical properties of that path will change.

![Diagram of the cross sectional area of the current carrying medium.](image)

Figure 2
Diagram of the cross sectional area of the current carrying medium. \((A)\)=cross sectional area, \((L)\)=length, \((\rho)\)= resistivity of the medium.

A decrease in the line width of the electrical path is the same as a decrease in the cross sectional area of the current carrying medium (Figure 2). Then from the relationship,

\[ R = \frac{\rho L}{A}, \]  
(Equation 1)
where \( \rho \) is the resistivity and \( L \) is the length\(^{13} \), as the cross sectional area \( A \) decreases, the resistance \( R \) increases. In the device, an increase of resistance beyond the engineered specifications may cause the entire device to fail or malfunction. The reverse of this idea holds true as well for an increase of line width (increase of cross sectional area).

The CD's of the device are defined by the mask and can be controlled by the amount of energy used to make the exposure. If a particular dark-bar on the mask is five microns in width, a "ideal" exposure would produce a five micron line in the resist and subsequently, a five micron line on the device. However, if more than the "ideal" exposure is used, the line width of the resist image will increase (for a positive resist). It is then apparent that the amount of exposure received by the resist is a critical parameter in the successful formation and control of CD's in the electronic device.

To fully understand the control of CD's, or the exposure in this case, something must first be known of the resists sensitivity. As in any photographic system, one attempts to expose the radiation sensitive material with the regions of the electromagnetic spectrum to which it is most sensitive. Matching the source's spectral output with the imaging medium's spectral sensitivity allows the most
efficient exposure use of a material. Exposure to non-actinic radiation is, of course, inconsequential.

It has been shown that a photoresist is not equally sensitive to different wavelengths of radiation\textsuperscript{14}. Hence, the region of the electromagnetic spectrum (deep UV, mid UV, near UV, or visible light) which is used will have a significant effect on both the resolving power\textsuperscript{15,16} and the amount of exposure as seen by the resist. Therefore, a fundamental parameter which must be considered is the spectral sensitivity of the photoresist.

Literature provides spectral absorbence and spectral transmittance data of photoresist\textsuperscript{17,18,19}. Spectral absorbence curves, however, typically display the percent absorbence per wavelength\textsuperscript{17}. Still another way of presenting spectral information of a photoresist is graphical representation of actinic absorption versus wavelength. The definition of actinic absorption is the difference between the absorbence of the photoresist before any exposure and the absorbence of the photoresist after an exposure\textsuperscript{20}. "Actinic absorbence is, however, more indicative of resist sensitivity than spectral absorbence"\textsuperscript{21}, in that it looks at the difference caused by the exposure. The difference between pre exposure and post exposure absorbence represents the spectral sensitivity of the photoresist. Still, none of these methods present the spectral sensitivity in absolute quantitative units. They
only lend themselves to a general qualitative statement of the resist's regions of sensitivity.

To determine the necessary exposure to produce some "desired result" (image), one would need to make a series of test exposures to determine the actual exposure for the resist and the source being used. For each resist and source combination, a series of exposures, varying the amount of exposure, are made with the resultant line widths plotted against the exposure. From this relationship, an exposure can be determined to produce a particular line width. As variations in the resist and source combination occur, a new set of exposure tests must be run. Each time the test is run for each resist and source combination, both valuable materials and valuable process-line time is lost.

In the semiconductor industry, exposures to resist can be made with a number of different sources (ie. mercury, duterium, or xenon; with narrow-band or wide-band passes), and each possibly, with different spectral radiation. The manufacturers typically provide quantitative information of the spectral radiation. If not, this information is easily measured with such instruments as a spectral radiometer or a thermopile.

However, if given the spectral sensitivity of the resist and the spectral radiation of the source, it is a simple task to determine the exposure time needed to
produce the desired results. The calculation can be made for both narrow-band sources and wide-band sources. If \( S_i(\lambda) \) denotes the spectral sensitivity of the resist in units of \( 1/\text{mJ/cm}^2 \) and \( H_i(\lambda) \) denotes the spectral radiation energy of the source in units of \( \text{mJ/cm}^2/\text{nm} \), then the broad-band sensitivity equals the following:

\[
S_b = \frac{\sum_\alpha^\beta S_i(\lambda) H_i(\lambda) \Delta \lambda}{\sum_\alpha^\beta H_i(\lambda) \Delta \lambda} \quad \text{(Equation 2)}
\]

where \( \alpha \) and \( \beta \) represent the extreme wavelengths of the broad-band in nanometers. This equation is derived from Van Kreveld's additivity law which states that the exposure, as a whole, is the sum of the fractional contributions at all wavelengths. By integrating the power of the source for the wavelength of interest, the following equation will yield the exposure time necessary to produce the desired results:

\[
t = \frac{1}{S_b H_t} \quad \text{(Equation 3)}
\]

where \( H_t \) denotes the integrated power of the source in \( \text{mW/cm}^2 \), and \( t \) denotes the exposure time in seconds.

If one's interest were only to a particular wavelength and not a band of wavelengths, it would be possible to use the following simplification of Equation 2 and 3:

\[
t = \frac{1}{S(\lambda) H(\lambda)} \quad \text{(Equation 4)}
\]

where only a single wavelength is considered.

Again, with a spectral sensitivity curve, one would only have to make the simple spectral radiometer measurement of the source, and run the same calculation as
before to determine the new exposure time for any changes that have occurred in the system. Using a spectral radiometer, for instance, one could make such a measurement between 250nm and 600nm, at 10nm increments, in less than five minutes time. Many processing schedules require more time than that just for one wafer or plate. It is easy to see how beneficial a spectral sensitivity curve is, not only in saving time and materials (money), but it also places one in a more versatile position to accommodate the need to change, adapt, or modify to the varying needs of the industry.

Information regarding spectral sensitivity allows photoresist users to quantitatively determine narrow-band and broad-band exposures and to predict other needs in making resist exposures. It offers a greater understanding of the resist and its characteristics (i.e. low intensity reciprocity law failure) and it promotes better educated decisions in choosing and purchasing exposing equipment.

The work presented here is a determination of the spectral sensitivity of KODAK Micro Positive Resist 820 (KMPR820). This choice of resist was made on the basis that it is a positive working resist with a wide exposure and process latitude. It has become widely accepted in the semiconductor industry, replacing many of the older type resists.
The methodology of the work is as follows. For a specific wavelength, a series of different exposures are made of a mask in a hard contact exposing system. The reason behind this hard contact exposing system is used to limit the amount of reflection and refraction which can take place between the two plates in physical contact. The greater the pressure of the contact, the lesser the space is between the plates and the lesser the possibility of reflection or refraction taking place. Matching the index of refractions for the resist and the substrate will also help in removing these effect. The materials which are used in this experiment are industry standards in which the highest care has been used to make the materials are the best they can be.

The mask used has equal line-space pairs of varying line widths. The exposed plate (with KMPR820) are developed and the line width of the resist images are measured. A relationship is drawn between the exposure needed to produce a line width, in much the same way as a characteristic curve relates the exposure needed to produce a density in conventional silver photography.

As noted before, as the amount of exposure increases, so does the width of a line (positive resist). If a space is critical, the opposite holds true, as exposure increases, the space width decreases. From this point forward, a line in the resist shall be termed a dark-bar.
and a space in the resist shall be termed a clear-bar. Clear-bars, then, increase with increased exposure and dark-bars decrease with increased exposure. This relationship between the exposure and the width of the image can be used to determine the amount of exposure needed to produce a desired image (clear-bars or dark-bars) width.

The definition for sensitivity is the inverse of the exposure needed to produce the desired result. This exposure shall be termed the speed point or speed point exposure. The desired result can be one of at least three different possibilities (Figure 3). First, the exposure necessary to reproduce 1:1 ratio of the mask line width to the chrome image line width of the sample. Second, the exposure necessary to reproduce a 1:1 ratio of the mask line width to the resist image line width of the sample.

![Diagram of three different criteria for determining the speed point exposure. A) 1:1 chrome to mask. B) 1:1 resist image to mask. C) 70° slope criteria.](image-url)
Third, the exposure necessary to produce a resist image with a bottom line width (of the sample) equal to that of the mask where the slope of the resist walls are approximately $70^\circ$ (if a right triangle were drawn with the resist thickness being the side opposite to the $70^\circ$ angle, and the bottom of the right triangle would be half of the extra width of image).

The third criterion for determining speed point has been used in this work. This criterion produces a line (dark-bar) in the resist which is larger than that of the mask image. When the substrate is etched away, the etchant also attacks the resist image. If the resist image were to be the same width as the mask image, the etching process would attack the resist image and reduce the width of that line. By making the line larger than the desired end result, the etching process attacks and reduces the resist line to the desired width.

A $70^\circ$ slope of the resist walls is used for two reasons. First, it is essentially impossible to produce a resist image with walls having $90^\circ$ slopes (anisotropic). It is typically sought to produce a line with walls of $60^\circ$ slope or better. These images work quite well through the remainder of the semiconductor fabrication process. In addition, the degree to which the walls are sloped can be tailored to meet the needs of a particular step in the fabrication.
The speed point exposure can be determined from the characteristic curve by working through the graph in the following manner. The exposure needed to produce the desired result is found as is shown in Figure 4. If the desired result is a line with a width of \( l_0 \) (microns), working backwards, the exposure needed to produce that result is \( E_0 \) (mj/cm\(^2\)).

**Figure 4**
Characteristic curve for a particular wavelength of the spectral band
The characteristic curve and speed point determination is performed for each wavelength band of interest. The sensitivity, which is the inverse of the speed point exposure, is plotted versus its corresponding wavelength to produce the final spectral sensitivity curve. These results are displayed in such a manner as to provide the user with the actual log sensitivity in units of \( \log(1/\text{mj/cm}^2) \) between 300nm to 500nm. With this, exposure time can be calculated for both narrow-band and broad-band sources.

It should be noted here, that there may exist a reciprocity law failure (RLF) with low intensity exposures. To date there has been no conclusive data, proving or disproving low intensity RLF of positive photoresists, in the literature\textsuperscript{24,25}.

However, it has been noted that there is image decay with a prolonged waiting period between the exposure and the processing. This may occur in order a few hours\textsuperscript{25}. A possible explanation for the image decay, is that the image (exposed resist), after a period of time, forms a compound which is not soluble in the developer (a basic solution). The net result of the exposure then, is zero.

Determining if low intensity RLF exists in KMPR820 is beyond the scope of this experiment, however, its existance was sought. If it does exist, to any great extent, the resulting data from this experiment may not be directly
useful for determining broad-band exposures. The data will, of course, still be directly useful for narrow-band exposure determination.

A guide line has been developed for photoresist users outlining a set of procedures and equipment requirements. The procedures allow the user to define standards for other photoresists in addition to "in-house" decisions regarding quality control of standards for incoming and outgoing products. Comment of the feasibility of this procedure for use by resist manufacturers follows in the conclusion.
II. EXPERIMENTAL

A. KMPR820 Samples

KODAK Micro Positive Resist 820 (KMPR820) was spun onto 60, 4-inch soda lime glass plates coated with chrome and a thin layer of anti-reflective chrome. The thickness of the KMPR820 was 0.5 microns +/- 0.005 microns. A 30 minute pre-bake at 90°C followed the spin coating.

B. MASK

The mask (Figure 5) designed for this experiment contains two sets of seven-bar, line/space pairs at 90° to each other and checkerboard patterns of varying line width.

![Figure 5](image-url)
The line/space pairs are of equal width. The line widths range between 50 microns and 0.5 microns (20 lp/mm and 1000 lp/mm respectively). The mask contains both light and dark fields with the line/space pairs numbered on the light field only.

This die is imaged across the entire face of the 5-inch, chrome-coated quartz plate. The resulting series of targets allows for a number of small area spectral exposures to be made of the mask during the experiment. Measurements were made of the mask to determine the variability of the line widths across the plate for the line/space pairs of interest.

C. Exposing System

A Schoeffel light source (1000 watt, xenon-lamp) was used with a Bausch & Lomb monochrometer in a hard contact exposing system. A 2700 grooves/mm grating and a 1350 grooves/mm grating were used in the monochrometer for UV and visible exposures respectively. The monochrometer produces a 9mm diameter spot of uniform radiance. Precision is within +/- 2nm at the peak of the energy distribution, and the band width is 10nm at 50% of the energy distribution. A Vincent Associates model 225X
shutter was used with GraLab timer to control the exposure time.

The exposing system was mounted on an Oriel optical bench. A sample chamber was constructed and mounted on the optical bench. It is used to produce pressure between the mask and the sample plate when in contact with one another.

D. Sample Chamber

The sample chamber (Figure 6), as described above, is essentially an open top box with an aperture in the front. From behind, a plate can be driven with a screw to apply pressure to a second plate via four heavy springs. This in

![Figure 6 Diagram of Sample Chamber](image-url)
turn, applies a uniform pressure to the mask and the sample plate which are in contact in the front of the box. The sample chamber has inside dimensions of 4" x 4" x 3". The open window is placed in the center front of the chamber and is 3" x 3" in size.

E. Spectral Exposures

The exposing system was set up such that the image plane was as close as possible to the source for maximum exposure energy. Figure 7 depicts the arrangement of the equipment on the optical bench (spacing enlarged for clarity). The appropriate gratings were placed in the

![Diagram](https://via.placeholder.com/150)

Figure 7
Exposure system
monochrometer and the intensity of the source at the image plane was measured for each wavelength of interest. A Hewlett Packard 8330A Radiant Flux Meter was used to make these measurements in \text{mw/cm}^2.

The monochrometer was set to a particular wavelength. The mask and the sample plate were placed into the sample chamber with the mask's chrome in contact with the samples' resist. Pressure was applied to the plates in excess of 20 pounds per square inch. The chamber was positioned for the first exposure (15 exposures possible per plate).

A series of exposures were made, typically between 50 \text{mj/cm}^2 and 150 \text{mj/cm}^2. For each exposure, the chamber was repositioned to a new area of resist. The pressure was then released upon completion and the plate was hand processed in KODAK Micro Positive Resist Developer 809 (diluted 1 part developer to 2 parts distilled water).

The developer was place into a 4 liter beaker which stood in a constant temperature water bath at 22^\circ\text{C} +/-0.5^\circ\text{C}. The plate was held horizontally with the resist coated side on top. A slow up-and-down motion was maintained during the 30 second development time to provide fresh developer to the image sites. A one minute distilled water rinse followed. The plate was dried with a nitrogen gun.

Random replications of the individual spectral exposures were made in the 260nm to 500nm range, at 20nm
increments. Also included, was the G, H, and I lines of the mercury spectrum. The replicated exposures were based on the original exposures, using finer increments near the exposures which produced the desired line width.

Line width measurements were made on an ITP-System 80 measuring microscope. Tests show this system to have a precision of +/-0.006 microns as compared to +/-0.038 microns of a VICKERS Image Shearing microscope.

The ITP-System 80 was set up to make measurements at the bottom of a resist line (see Appendix A for microscope program listing). The threshold of measurement was set to 50% (up the slope of the resist wall). This value was chosen because it produced consistent measureability throughout the experiment. The use of a lower threshold (measurement closer to the bottom of the resist line) made it impossible for the microscope to correctly focus on and measure many of the line widths.

Based on the definition of sensitivity for this work (described earlier), the following "desired result" was determined. Using the 70° slope criterion, and a 0.5 micron resist thickness, a 70° angle drawn from a perpendicular dropped below the edge of the mask image. This creates an increase of 0.14 microns on both sides of the resist image for a total of 0.28 microns. The desired result is a resist image 0.28 microns wider than the mask image from which it was formed (Figure 8).
F. Low Intensity Reciprocity Law Failure (RLF) Exposures

The following experiment was performed to begin to determine the extent to which low intensity RLF exists in KMPR820, if it exists at all.

Five-inch silicon wafers were spun coated with KMPR820. A S.V.P. Auto-Wafer-Processor was used with KODAK Micro Positive Resist Developer 933 (100%) for 20 seconds at 20°C. A 20 second deionized water rinse followed. An Optimetric Stepper was used as the exposing source (435nm).

An exposure series was made of a 5X reticle (resolution target) and an arbitrary exposure time was chosen. Exposures were stepped across three wafers with
this exposure energy. A particular line was measured throughout this experiment. This line width was measured and the average of these three wafers became the "optimum" line width of this "base" exposure.

The source was the attenuated with a 0.5 neutral density filter (measured with white light on a MacBeth 504 densitometer) and the new intensity was measured. A series of increased exposures were made to provide the "base" exposure and exposures of greater intensity. Replicates were made and the combined data, line widths and exposure energies, was modeled with a second order least squares polynomial. A predicted exposure, which would produce the "optimum" line, was calculated with the polynomial relationship.

This process was repeated for a second attenuation of the source, with 0.7 neutral density. The exposures were made, the data modeled with a second order least squares polynomial, and the predicted exposure calculated.
III. RESULTS

A. Mask Line Width Measurements

The ITP-System 80 microscope was set up for measuring chrome masks. The listing of this program is found in Appendix B. Two sets of dark-bars were measured.

The first set measured 1.70 microns with +/- 0.04 microns of variance across the mask. The second set was 4.67 microns with +/- 0.05 microns of variance across the mask.

B. Determination of "Desired Result"

The "desired result", as defined on pages 22 and 23, is a line width in the resist 0.28 microns greater than the line width of the mask's image. Then, for a 1.70 micron mask image, the desired result is a line in the resist 1.98 microns in width. The desired line width for the 4.67 micron mask image is a 4.95 micron line in the resist.

C. Intensity Measurement of Exposing Source

The measurement were made at the image plane with a correction filter for grating and a quartz plate to
represent the mask (no chrome). Measurements were made with both the UV and the visible grating. See Figure 9 for a graphical representation of these measurements.

![Spectral Output of Lamp](image)

**Figure 9**
Spectral intensity of xenon source

D. Spectral Exposures of 1.70 micron Mask Images

A computer program called Curve Fitter by Paul K. Warme © 1980 Interactive Microware was used to fit a second order least squares polynomial equation to the exposure energies and line width measurements. The exposures were regressed on the line widths. Table 1 displays the results of these least square regressions. Calculation of point estimates, given a line width, were performed by the
computer program. In this case, the exposure point estimates are calculated for a given line width of 1.98 microns. The 95% confidence intervals for both exposure point estimates and the calculated sensitivity values are presented. The characteristic curves (least square regression) are displayed in Appendix C.

Table 1
Results of 1.70 micron Image Measurements

<table>
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<th>( \lambda )</th>
<th>( b_0 )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( r )</th>
<th>( s )</th>
<th>Exposure (mJ/cm²)</th>
<th>log Sensitivity (log(mJ/cm²))</th>
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<td>1373.067</td>
<td>-414.663</td>
<td>.991</td>
<td>9.223</td>
<td>235.897 +/- 10.989</td>
<td>-2.373 +/- 0.020</td>
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<tr>
<td>300</td>
<td>2829.521</td>
<td>-2875.588</td>
<td>388.745</td>
<td>.942</td>
<td>34.815</td>
<td>244.120 +/- 18.749</td>
<td>-2.398 +/- 0.033</td>
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<tr>
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<td>175.934</td>
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<td>15.965</td>
<td>178.815 +/- 7.476</td>
<td>-2.252 +/- 0.018</td>
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<tr>
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<td>1415.321</td>
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<td>248.691</td>
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<td>6.851</td>
<td>126.490 +/- 6.952</td>
<td>-2.182 +/- 0.024</td>
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<td>11.494</td>
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<td>-1.944 +/- 0.026</td>
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<td>151.081</td>
<td>26.814</td>
<td>-26.213</td>
<td>.950</td>
<td>8.948</td>
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<td>-2.006 +/- 0.022</td>
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<td>405</td>
<td>244.088</td>
<td>-67.266</td>
<td>-5.655</td>
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<td>7.195</td>
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<td>211.236 +/- 17.126</td>
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<td>-233.530</td>
<td>18.265</td>
<td>.903</td>
<td>27.977</td>
<td>196.765 +/- 13.568</td>
<td>-2.294 +/- 0.038</td>
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greater than 1068.8 less than -3.03

greater than 1872.0 less than -3.27

greater than 2385.0 less than -3.38

No sensitivity values were determined for the spectral exposures at 460nm, 480nm, and 500nm. Exposure times were in excess of 10 minutes without reaching the desired line width. These wavelengths will be represented by a dotted line in the spectral sensitivity plot to indicate that the sensitivity is less than the values reported.
Table 2 is the tabulation of work similar to that of Table 1, where images produced by a 4.67 micron line were measured. The characteristic curves for these least squares regressions are found in Appendix D.

Table-2
Results of 4.67 micron Image Measurements

<table>
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<tr>
<th>λ</th>
<th>b₀</th>
<th>b₁</th>
<th>b₂</th>
<th>r</th>
<th>s</th>
<th>Exposure (mj/cm²)</th>
<th>log Sensitivity (log(mj/cm²))</th>
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<tbody>
<tr>
<td>360</td>
<td>-21327.154</td>
<td>9432.658</td>
<td>-1022.718</td>
<td>.921</td>
<td>28.999</td>
<td>305.322 +/- 21.167</td>
<td>-2.485 +/- 0.030</td>
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<tr>
<td>320</td>
<td>60189.149</td>
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<td>2332.985</td>
<td>.602</td>
<td>25.644</td>
<td>201.303 +/- 25.892</td>
<td>-2.384 +/- 0.056</td>
</tr>
<tr>
<td>340</td>
<td>4936.042</td>
<td>-1733.423</td>
<td>153.538</td>
<td>.992</td>
<td>7.329</td>
<td>177.678 +/- 5.737</td>
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</tr>
<tr>
<td>365</td>
<td>2227.168</td>
<td>-687.699</td>
<td>52.522</td>
<td>.961</td>
<td>8.592</td>
<td>109.977 +/- 6.021</td>
<td>-2.841 +/- 0.027</td>
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<tr>
<td>380</td>
<td>7381.312</td>
<td>-2719.980</td>
<td>251.877</td>
<td>.967</td>
<td>8.091</td>
<td>98.130 +/- 4.116</td>
<td>-1.955 +/- 0.028</td>
</tr>
<tr>
<td>420</td>
<td>-1097.705</td>
<td>645.820</td>
<td>-85.988</td>
<td>.870</td>
<td>19.309</td>
<td>235.722 +/- 28.996</td>
<td>-2.377 +/- 0.039</td>
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</table>

E. Low Intensity Reciprocity Law Failure Study

The intensity of the source without attenuation was measured to be 316 mw/cm² by an OAI meter and probe. With the 0.5 and 0.7 neutral density filters, the attenuated intensity was 80 mw/cm² and 45 mw/cm² respectively.

The "base" exposure (no attenuation) was chosen to be 71.1 mj/cm² at a 0.225 second exposure time. Three wafers were exposed with this "base" exposure to obtain an optimum line width of 3.640 microns with +/- 0.41 microns of
variation across a wafer and +/- 0.10 microns between wafers.

The attenuated exposures were made and line widths measured. The second order least squares polynomial regression was calculated and is displayed in Appendix E. The calculated point estimates (exposure) based on a 3.640 micron line are 104.6 mJ/cm² (+/- 4.2 mJ/cm²) and 101.7 mJ/cm² (+/- 2.6 mJ/cm²) for the 0.5 and 0.7 neutral density filters respectively. With 95% confidence intervals, these exposures are not significantly different. They are, however, significantly different from the "base" exposure of 71.1 mJ/cm².
IV. DISCUSSION

A. Visual Inspection of Least Square Regressions

Visual inspection fails to reject the relationships indicated by the majority of least squares polynomial fit of the data which comprises the characteristic curves. The exceptions to this are the 420nm characteristic curves for both the 1.70 micron images and the 4.67 micron images and the 320nm characteristic curve for the 4.67 micron images. In these cases, the fitted curves do not obviously represent the data.

B. Correlation Coefficient Tests

The correlation coefficient \( r \) was tested in each regression for significance against a critical \( r \) value. If the calculated \( r \) is greater than the critical \( r \), then the correlation of the regression is significant or acceptable. In only one regression is this not the case. The \( r \) value of the 320nm characteristic curve, when a 4.67 micron image is used, fails this test. This means that the correlation of this regression may not be significant and the exposure point estimate, therefore, will not be used in any further
analysis. The remaining exposure point estimates (speed points) will be considered valid and will be used.

C. Spectral Sensitivity

During the course of this investigation, spectral sensitivity data was furnished by Eastman Kodak for their KMPR820\textsuperscript{26}. Their definition of sensitivity is again, the inverse of the exposure ($\text{mJ/cm}^2$) needed to produce the "desired result". However, in this case the desired result was the sibalization of a 1.0 micron thick area of resist. This is different from the desired result of this work. It is expected that the exposure energy needed to clear out an area of resist 1.0 micron thick is less than the exposure energy needed to form a desired line width\textsuperscript{27,28}.

Therefore, it is expected that the spectral sensitivity reported in this investigation will be less than those reported by KODAK. Figure 10 is a graphical comparison of the reported spectral sensitivity of this and of KODAK.

Figure 10 clearly indicates that there is a significant difference in reported sensitivities for all wavelengths and that this difference is in the expected direction.
Factors which might affect the reported sensitivity values are resist thickness, developer and its dilution, and the definition of sensitivity used. Table 3 lists each of these parameters for both works, separated by a greater than or less than symbol which indicates the work which would be expected to show greater sensitivity.

Table 3
Comparison of Sensitivity Values

<table>
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<th>KODAK</th>
<th>HUCK</th>
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<tbody>
<tr>
<td>definition</td>
<td>energy to sibilize 1 micron thick area</td>
<td>&gt;</td>
</tr>
<tr>
<td>developer</td>
<td>KMPD 809</td>
<td>&gt;</td>
</tr>
<tr>
<td>dilution</td>
<td>2:3</td>
<td>&gt;</td>
</tr>
<tr>
<td>resist thickness</td>
<td>1.0 microns</td>
<td>&lt;</td>
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</table>
Two of these parameters are in favor of the results shown in Figure 10. The magnitude to which each of the parameters in Table 3 affects the sensitivity values is undetermined. However, to the best of the Author's ability, these parameters are placed in decending order of magnitude. It is not surprising then, that the spectral sensitivity values determined in this investigation are less than those reported by KODAK.

Figure 11 graphically presents the comparison between sensitivity values based on the measurement of a resist line reproduced by a 1.70 micron and a 4.67 micron mask image.

![Graph showing comparison of sensitivities based on 1.70 and 4.67 micron images](image)
A Chi Square Test was performed on the above data. It concluded a lack of good fit for these two curves. However, when the data points at 300nm were removed, the Chi Square test resulted with a good fit of the two curves. Therefore, at only one wavelength (of those studied) do the two methods of determining sensitivity significantly differ. There is not enough information to predict that this difference is a general trend for the shorter wavelengths.

D. Low Intensity RLF

The reciprocity curve (Figure 12) indicates a significant deviation from a zero reciprocity law failure.
line for low intensity exposures. It is apparent that low intensity reciprocity law failure exists in KMPR820 for intensities of approximately 100 mW/cm² and below.

E. Suggested Procedures

The procedures used in the experiment are, for the most part, sound. A source with greater intensity would increase the efficiency of the work and might remove the affect of low intensity RLF.

Although not studied here, it is suggested that the time period between the resist exposure and resist development may have an affect on the speed or sensitivity of the resist through a process of image decay. The end product of the desired reaction, the indenecarboxycylic acid, may further react to form an undesired, non-soluble compound. The duration between exposure and development should be kept to a minimum.

F. Feasibility

The determination of sensitivity based on exposure versus line widths is a workable method. This method seems to generally correlate with the method used by KODAK where
exposure was related to clearing a 1.0 micron thick area of resist.

The procedures used in this investigation for the determination of spectral sensitivity are likewise practical. The use of a source with greater intensity is advisable. Until further work is accomplished in defining a standard method of determining sensitivity or speed, the investigator or user is at liberty to choose a definition. The definition investigated in this work can be used to compare with other definitions to reach a final, standardized method for determining spectral sensitivity of a photoresist.

The use of a wedge spectrograph could facilitate the entire exposing procedures by placing more information of a range of wavelengths onto the resist. The fabrication of a target for this system should include varying line/space patterns and varying density areas. For one overall exposure, this would allow a number of different effective exposures to be made to the resist and would allow the user to base results on line width measurements or loss of resist thickness measurements.
V. CONCLUSIONS

Failure to disprove the significance of the least square regressions and the exposure point estimates leads to Figure 13, the spectral sensitivity of KODAK Micro Positive Resist 820, given the following parameters.

The definition of sensitivity is the inverse of the exposure needed to produce a line width 0.28 microns (70° wall slope criterion) greater than that of the mask image used in a hard contact exposing system. Development of the 0.5 micron thick resist is carried out in KODAK Micro Positive Resist Developer 809, diluted 1 part developer to 2 parts distilled water at 22°C for 30 seconds.

![Figure 13](Image)

**Figure 13**
Spectral Sensitivity of KMPR820
No significant difference was found between the calculated sensitivities based on the measurement of a resist line produced by either a 1.70 micron image or a 4.67 micron image. Therefore, for the range investigated, sensitivity is not dependent on the width of the line used for the measurement. No attempts were made to extrapolate outside of this range for larger or smaller line widths clearly beyond the scope of this work.

Low intensity reciprocity law failure exist with exposure intensities of approximately 100mW/cm² and lower in KMPR820.

Many of the reported sensitivity values in Table 1, Table 2, and Figure 12 are based on exposures with intensities well below 100mW/cm². These exposures are assumed to be affected by reciprocity as well. It is therefore suggested, that the reported spectral sensitivity values not be used to calculate a broad-band source exposure unless the integrated intensity of the broad-band source is of the range used in this investigation (approximately 4mW/cm² or less). Typically, this is not the case. Most broad-band sources are of intensities much greater than this.

Suggestions For Future Work

A continuation of the investigation of low intensity reciprocity law failure is needed in order to conclusively
determine the useful extent to which this and similar spectral sensitivity information can be used in broad-band exposure determinations.

A continuation of the study of sensitivity versus the width of the line used in the calculations beyond the 1.70 micron and 4.67 micron line width range is needed. This may lead to a better understanding of the differences between the definitions of sensitivity stated within this work.

The need for a standard definition of sensitivity (or speed) of a photoresist is apparent. Without it, any number of sensitivity values can be reported for the same photoresist leading to confusion and costly errors in an industry where accuracy is critical. It is paramount that a standard definition for photoresist sensitivity be developed which is applicable to the wide range of situations encountered in the semiconductor industry.
VI. REFERENCES


22 Personal notes from Advanced Sensitometry at Rochester Institute of Technology, January, 1981.


### Appendix A.

**Bottom line setup**

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### Appendix B.

**Chrome mask setup**

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<td>Focus sensor 34</td>
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Appendix C. Characteristic Curves for 1.70 micron Images

- 300nm

- 320nm

- 340nm

- 360nm

exposure (mj/cm² x 10)

line width (microns x 10⁻¹)
Appendix C. continued

- **365 nm**
  - Exposure vs. line width (microns $\times 10^{-1}$)

- **380 nm**
  - Exposure vs. line width (microns $\times 10^{-1}$)

- **400 nm**
  - Exposure vs. line width (microns $\times 10^{-1}$)

- **405 nm**
  - Exposure vs. line width (microns $\times 10^{-1}$)
Appendix C. continued

![Graph 1](420nm)

- Exposure (mJ/cm² x 10)
- Line width (microns x 10⁻¹)

![Graph 2](436nm)

- Exposure (mJ/cm² x 10)
- Line width (microns x 10⁻¹)
Appendix D. Characteristic Curves for 4.67 micron Images

- **300nm**
  - Exposure (mJ/cm² x 10)
  - Line width (microns x 10⁻²)

- **320nm**
  - Exposure (mJ/cm² x 10)
  - Line width (microns x 10⁻¹)

- **340nm**
  - Exposure (mJ/cm² x 10)
  - Line width (microns x 10⁻¹)

- **365nm**
  - Exposure (mJ/cm² x 10)
  - Line width (microns x 10⁻¹)
Appendix D. continued

![Graphs showing exposure vs. line width for 380nm and 420nm wavelengths.](image)
Appendix E. Characteristic Curves for RLF work

0.5 ND filter

0.7 ND filter
Vita

Matthew Ludwig Huck was born and raised in the Syracuse, New York area. From Cicero High School, Matthew went to Rochester, New York to pursue a Bachelor of Science degree in Photographic Science and Instrumentation at Rochester Institute of Technology.

The summer prior to his fourth year was spent working in the semiconductor field with American Microsystems, Inc., in Santa Clara, California. His main responsibilities were in the mask making area and he was able to attend a course given on the topic of Semiconductor Fabrication on his spare time. The origin of his thesis began while at AMI. During his senior year, Matthew was one of three recipients for the Fuji Scholarship Awards.

The thesis is a requirement for the Bachelor's degree in Photographic Science and Instrumentation. Upon graduation, Matthew will return to AMI and pursue a career in the field of semiconductor fabrication.