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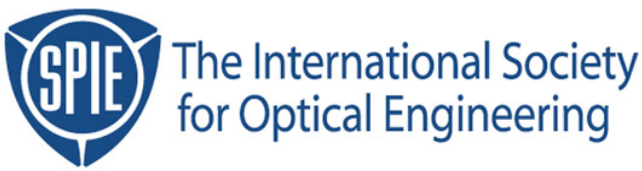

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A FT-IR Method to Determine Dill's C Parameter for DNQ/Novolac Resists with E-beam and I-line Exposure

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ABSTRACT

Typically, the Dill ABC parameters for optical resists are determined by coating a resist on a nonreflecting substrate and then measuring the change in the intensity of transmitted light at the wavelength of interest as a function of incident energy. Resist absorbance may not be selective in isolating and measuring only the photoactive species, and in some cases changes in absorbance can not be directly correlated to changes in the concentration of the photoactive species. FT-IR spectroscopy can directly measure changes in the photoactive species by isolating and measuring absorbance peaks unique to the photoactive species. FT-IR, employed in reflectance mode, is not constrained to transparent substrates, but can instead be used with silicon wafers or chrome coated quartz plates. The ability to use these substrates is important when determining Dill's C parameter under e-beam exposure where the degree of back-scattered electrons is dependent on the underlying substrate, and the use of quartz is prohibited due to charging considerations. Dill's C parameter is determined for a variety of commercial i-line resists under both e-beam and i-line exposure. The ProABC software, a lithography simulator that extracts ABC parameters through a best fit of model to data, is employed to extract Dill's C parameter. This software has been specially modified to allow FT-IR absorbance input.

Keywords: Dill C parameter, DNQ/novolac resist, FT-IR, electron beam, i-line

1. INTRODUCTION

Lithography simulation has become an important tool for research, development and manufacturing applications in semiconductor fabrication[1]. In many cases the accuracy of such simulation is limited not so much by the models themselves but by the accuracy of the input parameters used by the models. Although many modeling input parameters represent easily determined physical quantities such as a lens numerical aperture or beam voltage, others describe difficult to measure properties such as resist kinetic rate constants. One such parameter is the kinetic rate constant of the first order exposure reaction of a photoresist, the so-called Dill's C parameter[2]. A photosenitive component of the photoresist, called a photoactive compound (PAC) or a photoacid generator (PAG), undergoes a first order photochemical decomposition to some product (typically an acid) as a function of *E*, the dose incident on the PAC molecules.

$$\frac{\partial m}{\partial E} = -Cm \tag{1}$$

where m is the relative concentration of the photosensitizer and C is the exposure rate constant[1,2]. Note that the exposure dose E represents the dose incident on the PAC molecules themselves and may not be equal to the dose incident on the top of a thin film of photoresist. Equation (1) has an obvious solution.

$$m = e^{-CE} \tag{2}$$

Complications arise, however, because generally only the incident dose, not the actual dose in the photoresist, is known. Simulation is typically used to calculate the dose inside the resist film as a function of the incident dose.

Measurement of the Dill C parameter typically involves measurement of some physical quantity directly proportional to *m* as a function of incident dose. Then, using simulation to convert incident dose to actual dose, a best fit of equation (2) to the data yields the rate constant C[3]. The most common measurement technique for optical resists, first proposed by Dill, is to measure the absorbance of the resist film at the actinic wavelength *in situ* during exposure. Changes in *m* are directly proportional to changes in the absorbance. However, resist absorbance at the actinic wavelength may not be selective in isolating and measuring only the photoactive species, and in some cases changes in absorbance cannot be directly correlated to changes in the concentration of the photoactive species. FT-IR spectroscopy can directly measure changes in the photoactive species by isolating and measuring absorbance peaks unique to the photoactive species. FT-IR, by employing reflectance mode measurement, is not constrained to transparent substrates, but can instead be used with silicon wafers or chrome coated quartz plates. The ability to use these substrates is important when determining Dill's C parameter under e-beam exposure where the degree of back-scattered electrons is dependent on the underlying substrate, and the use of quartz is prohibited due to charging considerations. The ProABC software[3], a lithography simulator that extracts ABC parameters through a best fit of model to data, is employed to extract Dill's C parameter. This software has been specially modified to allow FT-IR absorbance input.

2. EXPERIMENTAL

Electron beam written substrates were either 4-inch synthetic quartz wafers coated with 105 nm of AR3 antireflective chrome, 4-inch silicon wafers, or 4-inch silicon wafers coated with 100 nm of evaporated aluminum. I-line substrates were either 6-inch silicon wafers or 6-inch silicon wafers coated with 100 nm of sputtered aluminum. Resists were seven DNQ/novolac based resists that are available commercially from a variety of resist suppliers. A list of suppliers and resists is presented in Table 1. All resists were coated to approximately 600 nm by spin casting from 2000 to 4000 RPM. The resist postapply bake was 95°C for 60 seconds and no postexposure bake was employed.

All e-beam exposures were with a JEOL JBX-5DII e-beam tool operating at 50 kV. An array of 1 mm x 1 mm squares was exposed with an e-beam at various doses and then the DNQ (the photosensitizer for these resists) absorbance at ~2100 cm^{-1} was measured using FT-IR. All i-line exposures were with a 0.45 NA GCA Autostep 200. For the i-line exposures, an array of 3 mm x 25 mm rectangles was exposed at various doses and then the DNQ absorbance at ~2100 cm^{-1} was measured using FT-IR.

FT-IR measurements were made with a Brucker Equinox 55 FT-IR employing an IRscope II in reflectance mode on either resist coated silicon or chrome on synthetic quartz. Resist thickness was 600 nm, spectral resolution was 4 cm^{-1} and typically 64 spectra were averaged from each exposure measurement. A typical experiment was to fully expose an area on the wafer some distance from the exposure pattern with the microscope's white light illuminator for 5 minutes. This time interval insured that no unexposed DNQ remained, a fact that was confirmed by showing that the subtractive spectra between 5 and 6 minutes was flat in the 2100 cm^{-1} region showing that no additional photochemistry was occurring. The fully exposed spectra were employed as reference spectra. The Brucker Opus software which controlled the spectrometer data acquisition and IRscope II allowed one to measure a predetermined matrix of locations, which in our case corresponded to the location of either e-beam or i-line exposure. The FT-IR reference signal was subtracted from the exposed area signal and integrated from 2045 cm^{-1} to 2206 cm^{-1}. The FT-IR absorbance was normalized to the absorbance of the unexposed resist film. The exposure rate constant was determined through a best fit of equation (2).

For the electron beam measurements, the ProBEAM/3D lithography simulator was employed to predict the absorbed resist dose as a function of depth into the resist for a given incident dose. This value is used to convert the Dill C parameter from units of $cm^2/\mu C$, the traditional units associated with incident dose, to units of cm^3/J, the latter accounting for the absorbed dose within the resist. With 50 kV e-beam exposure this absorbed dose changes little as a function of depth into the resist, and the calculated values at all resist depths were averaged to give a conversion factor of 6.92 J/μC-cm for chrome on silicon dioxide, 6.89 J/μC-cm for silicon, and 6.64 J/μC-cm for aluminum on silicon.

3. RESULTS AND DISCUSSION

Traditional measurement of the Dill ABC parameters is accomplished by exposing the resist on a transparent substrate and constantly measuring the intensity of the light transmitted. The transmitted intensity as of function of exposure dose is then analyzed to determine the resist ABC parameters. Determining the Dill ABC parameters by this method requires that the photoresist change its optical properties with exposure. While the Dill ABC parameters are important for defining the optical image within the resist as it varies with optical exposure, the same parameters are also employed to determine the resist latent image. It is in determining the resist latent image that difficulties can arise. Resist absorbance at any specific wavelength may not be selective in isolating and measuring only the photoactive species, and in some cases changes in absorbance cannot be directly correlated to changes in the concentration of the photoactive species. In DNQ/novolac resists, the A and C values of absorbance directly relate to DNQ concentration, while in chemically amplified (CA) resists the changes in resist absorbance often does not reflect PAC decomposition, but instead other photochemical transformations such as quinone formation. With non-optical exposure such as x-ray or e-beam, no change in absorbance occurs, and changes in DNQ or PAC must be obtained by some other method. While the concept of Dill ABC parameters will retain value for defining the resist image and exposure kinetics in optical resists, a direct measurement of PAC decomposition and acid production is needed for CAR resists and for non-optical exposures.

FT-IR spectroscopy can directly measure changes in the photoactive species by isolating and measuring absorbance peaks unique to the photoactive species. Reflectance mode FT-IR is not constrained to transparent substrates, but can instead be used with silicon wafers or chrome coated quartz plates. The ability to use these substrates is important when determining Dill's C parameter under e-beam exposure where the degree of back-scattered electrons is dependent on the underlying substrate, and the use of quartz is prohibited due to resist charging during the e-beam writing time, resulting in dose errors. In addition, antireflective coatings which are transparent to the FT-IR wavelength being monitored can be employed, which mitigates the effect of small changes in resist thickness on the calculated C value during optical exposure.

We employed two methods to determine Dill's C parameter for a variety of commercial i-line resists under both e-beam and i-line exposure. This was accomplished by exposing the resist and integrating the DNQ diazide absorbance at 2100 cm^{-1}. A typical FT-IR spectrum of a DNQ/novolac resist showing the change in the absorbance at ~2100 cm^{-1} as a function of exposure time is seen in Figure 1. Illumination was with the white light illuminator of the microscope and is given in seconds. The spectra shown are the difference of the spectra taken at different exposure times subtracted from the unexposed spectra. The scale is adjusted for clarity to show the absolute value of the change in absorbance. During exposure the absorbance between 2045 and 2206 cm^{-1} decreases, reflecting a decrease in DNQ concentration.

With 50 kV e-beam exposure, where the deposited exposure dose is constant through the resist, the exposure rate constant can be determined through a best fit of equation (2). The ProABC software, a lithography simulator that extracts ABC parameters through a best fit of model to data, is employed to extract Dill's C parameter. This software has been specially modified to allow FT-IR absorbance input. With i-line exposure, where the deposited exposure dose is not constant through the resist, the ProABC software can successfully extract the Dill C parameter by first modeling this energy distribution during exposure.

3.1 Dill C parameter for e-beam exposure

Most commercial i-line resists have had their Dill parameters measured for i-line exposure, and these values are readily available. Unfortunately, little published work is available describing Dill parameters for resists under e-beam exposure. The determination of the e-beam Dill C parameter, a measure of exposure kinetics, is not readily obtained by traditional UV measurement methods. We therefore undertook the task of developing a new method to determine the Dill C parameters for resists with 50 kV e-beam exposure.

We have developed a new and versatile FT-IR method to determine Dill's C parameter and have employed that method to determine C for all seven resists under evaluation. All DNQ/novolac resists contain a diazide moiety on the PAC species, and it is this diazide functionality that initiates the photochemical rearrangement that transforms the DNQ to an indene carboxylic acid. The diazide moiety has a unique infrared absorbance at about 2100 cm^{-1} that

can be easily monitored with little interference from other PAC or polymer functionality. The FT-IR data acquisition was performed in reflection mode which necessitates that an IR reflective substrate is present under the resist film. Silicon, aluminum, and chrome are reflective in the IR to a sufficient degree to allow for operation of the IR in reflective mode. All three materials are also sufficiently conductive to allow for e-beam exposure of 600 nm thick resist films without resist charging causing dose errors.

A typical experiment to determine the Dill C parameter was to coat a wafer with 600-nm of resist and expose a dose matrix. The normalized IR absorbency as a function of exposure dose was determined and the best fit of equation (2) yielded the Dill C value in terms of $cm^2/\mu C$. An example of the decrease in IR absorbance as a function of exposure dose for SPR700 with e-beam exposure on a chrome coated silicon dioxide wafer is presented in Figure 2. All resists gave similar plots with very good fits to equation (2). Values for C measured on chrome on quartz substrates are presented in Table 1 in both units of $cm^2/\mu C$, the traditional units associated with Dill's C parameter, and in units of cm^3/J, the latter accounting for the absorbed dose within the resist. Parameter input into ProBEAM/3D requires the units to be in the form of cm^3/J, and the conversion factor has been determined via ProBEAM/3D simulation of an open field exposure.

The Dill C value in terms of incident dose ranges from 0.0061 to 0.0092 $cm^2/\mu C$ for the seven resists measured, although most resists fall in a relatively small range from 0.0070 to 0.0079 $cm^2/\mu C$. It is not clear why the Dill C parameters for the Shipley and Clariant resists are significantly lower and higher respectively than the values observed for the remaining five resists which all cluster rather tightly. The standard error associated with determining the Dill C value on chrome coated silicon dioxide is quite low and ranges from 1% to 2% for all seven resists. This small error allows one to say with confidence that the Shipley and Clariant resists show different PAC decomposition behavior than the other resists with e-beam exposure.

Table 1. Dill C parameters determined for DNQ/novolac resists exposed with a 50 kV electron beam on a chrome coated silicon dioxide substrate. The Dill C is determined by a best fit to the equation $m = e^{-CE}$.

Manufacturer	Resist	Dill C ($cm^2/\mu C$)	Error ($cm^2/\mu C$)	Dill C (cm^3/J)
Clariant	AZ5204	0.0092	± 0.00012	0.00133
JSR	IX420H	0.0072	± 0.00013	0.00106
Olin	OiR 907-12	0.0073	± 0.00014	0.00110
Shipley	SPR700	0.0061	± 0.00010	0.00097
Sumitomo	PFM-10A4	0.0070	± 0.00014	0.00106
TOK	OEBR2000	0.0079	± 0.00014	0.00116
Nippon Zeon	ZMP	0.0070	± 0.00011	0.00103

Two other substrates were employed to determine the e-beam Dill C parameter for the seven i-line resists. An example of the decrease in IR absorbance as a function of exposure dose for SPR700 with e-beam exposure on an aluminum coated silicon wafer is presented in Figure 3. All resists gave similar plots with very good fits. Values for C measured on aluminum on silicon substrates are presented in Table 2 in both units of $cm^2/\mu C$ and cm^3/J.

The Dill C value in terms of incident dose ranges from 0.0069 to 0.0095 $cm^2/\mu C$ for the seven resists measured, although most resists fall in a relatively small range from 0.0073 to 0.0080 $cm^2/\mu C$. Like the chrome on silicon dioxide results, the Dill C parameters for the Shipley and Clariant resists are significantly lower and higher respectively than the values observed for the remaining five resists which all cluster rather tightly. The standard error associated with determining the Dill C value on chrome coated silicon dioxide again is quite low and ranges from 1% to 2% for all seven resists. As expected, comparison of the values in Tables 1 and 2 shows that the extracted C values do not show a discernible substrate dependence.

Table 2. Dill C parameters determined for DNQ/novolac resists exposed with a 50 kV electron beam on an aluminum coated silicon substrate. The Dill C is determined by a best fit to the equation $m = e^{-CE}$.

Manufacturer	Resist	Dill C ($cm^2/\mu C$)	Error ($cm^2/\mu C$)	Dill C (cm^3/J)
Clariant	AZ5204	0.0095	± 0.00014	0.00143
JSR	IX420H	0.0073	± 0.00013	0.00110
Olin	OiR 907-12	0.0076	± 0.00011	0.00115
Shipley	SPR700	0.0069	± 0.00008	0.00104
Sumitomo	PFM-10A4	0.0073	± 0.00012	0.00110
TOK	OEBR2000	0.0080	± 0.00009	0.00121
Nippon Zeon	ZMP	0.0071	± 0.00008	0.00107

The final substrate employed to determine the Dill C parameter for the seven i-line resists was bare silicon. An example of the decrease in IR absorbance as a function of exposure dose for SPR700 with e-beam exposure on a silicon wafer is presented in Figure 4. All resists gave similar plots with relatively poor fits. Values for C measured on silicon substrates are presented in Table 3 in both units of $cm^2/\mu C$ and cm^3/J.

The Dill C value in terms of incident dose ranges from 0.0057 to 0.0088 $cm^2/\mu C$ for the seven resists measured with none of the tight clustering of values seen on chrome or aluminum. The standard error associated with determining the Dill C value on silicon is much higher compared to the other two substrates and ranges from 5% to 25% for the seven resists. This large error is due in part to the poor fit at higher exposure doses when most of the PAC has decomposed. Silicon, unlike chrome and aluminum, is not highly reflective in the IR. Instead, some of the IR is transmitted through the silicon and is subsequently reflected by the metal microscope stage. This reflection sets up IR standing waves in the silicon and also the coated resist, causing interference in measuring low PAC values. This is due to difficulty in assigning a reference absorbance as well as integrating the standing waves along with the actual IR absorbance. This interference is not seen with substrates, such as chrome and aluminum, which do not transmit in the IR and as such are preferred for determining PAC concentration by this method.

Table 3. Dill C parameters determined for DNQ/novolac resists exposed with a 50 kV electron beam on a silicon substrate. The Dill C is determined by a best fit to the equation $m = e^{-CE}$.

Manufacturer	Resist	Dill C ($cm^2/\mu C$)	Error ($cm^2/\mu C$)	Dill C (cm^3/J)
Clariant	AZ5204	0.0088	± 0.00050	0.00128
JSR	IX420H	0.0075	± 0.00182	0.00109
Olin	OiR 907-12	0.0083	± 0.00064	0.00121
Shipley	SPR700	0.0083	± 0.00064	0.00121
Sumitomo	PFM-10A4	0.0057	± 0.00055	0.00083
TOK	OEBR2000	0.0081	± 0.00090	0.00118
Nippon Zeon	ZMP	0.0070	± 0.00159	0.00102

3.2 Dill C parameter for i-line exposure

We have also employed this new FT-IR method to determine Dill's C parameter under i-line exposure. The FT-IR data acquisition was performed in reflection mode with the resist coated on an aluminum coated silicon wafer. The need for an IR reflective substrate and the relative ease of preparation makes aluminum a good choice for coating silicon for all FT-IR measurements.

A typical experiment to determine the Dill C parameter was to coat a wafer with 600 nm of resist and expose a dose matrix. The normalized IR absorbency as a function of exposure dose was determined just as for the e-beam exposure case. An example of the decrease in IR absorbance as a function of exposure dose for SPR700 with i-line exposure on an aluminum coated silicon wafer is presented in Figure 5.

Unlike e-beam exposure, the i-line exposure will give energy distributions that vary considerably through the thickness of the resist. Thus, the relative PAC concentration *m* will also vary considerably through the depth of the resist. Since an FT-IR measurement relates absorption to an average PAC value through the film thickness, careful consideration of this energy distribution through the resist is required to properly deconvolve the C value from these average PAC concentration measurements. Use of a highly reflective substrate such as aluminum means that energy distributions are even more strongly thickness dependent due to the formation of standing waves in the resist during i-line exposure. The ProABC program was used to model the exposure on a reflective substrate and extract the best fit C value to the average PAC concentration data. Figure 5 shows an example of the measured FT-IR data compared to the ProABC best fit, giving a C value of 0.062 cm^2/mJ. Note that the GCA Autostep used for the exposures does not use a standard calibrated dose measurement and produces a dose to clear for this resist of about 30 mJ/cm^2.

The use of equations (1) and (2) differs between e-beam and optical lithography simulations in that the e-beam case uses deposited energy per unit volume and the optical lithography case uses energy per unit area. The difference is straightforward since the optical absorption coefficient of the resist relates energy per unit area to deposited energy per unit volume[4]. Thus, the exposure rate constant *C* for electron beam exposure is roughly equivalent to the optical *C* divided by the resist optical absorption coefficient α. As an order of magnitude analysis, suppose an optical resist exhibits C ~ 0.024 cm^2/mJ and $\alpha \sim 0.8\ \mu m^{-1}$. Thus, the e-beam equivalent value of *C* (for the same effective resist sensitivity) would be about 0.003 cm^3/J. From the data presented here it is obvious that the i-line resists studied have a much lower sensitivity to electron exposure than to optical exposure, as one might expect.

4. CONCLUSIONS

A method to quickly determine the Dill C parameter for commercial i-line resists under e-beam and i-line exposure was described. This was accomplished by determining IR absorbance of the diazide moiety at 2100 cm^{-1} as a function of exposure dose in resist films, and either determining the best fit of the data to the equation $m = e^{-CE}$ or employing ProABC to determine a best modeled fit of the data.

The Dill C parameter was determined for seven commercial i-line resists under 50 kV e-beam exposure. Values for C were measured on chrome on quartz substrates in both units of $cm^2/\mu C$, the traditional units associated with Dill's C parameter, and in units of cm^3/J, the latter accounting for the absorbed dose within the resist. For i-line exposure, the strong standing waves necessitated the use of modeling to extract the C parameter. However, swing curve effects and their dependence on the resist refractive index make this approach sensitive to experimental error and error in parameters used for the data analysis. Future work will use an IR transparent i-line antireflective coating on top of the aluminum to reduce these effects.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. C. A. Mack, Inside PROLITH: A Comprehensive Guide to Optical Lithography Simulation, FINLE Technologies (Austin, TX: 1997).

2. F. H. Dill, W. P. Hornberger, P. S. Hauge, and J. M. Shaw, "Characterization of Positive Photoresist," *IEEE Trans. Electron Devices*, **ED-22** (1975) pp. 445-452.

3. C. A. Mack, T. Matsuzawa, A. Sekiguchi, and Y. Minami, "Resist Metrology for Lithography Simulation, Part 1: Exposure Parameter Measurements," *Metrology, Inspection, and Process Control for Microlithography X, Proc., SPIE*, **2725** (1996) pp. 34-48.

4. A. R. Neureuther, M. Zuniga, and N. Rau, "Modeling of the Patterning Process with Chemically-Amplified Resists," *Microprocess and Nanotechnology '97* (1997).

FIGURES

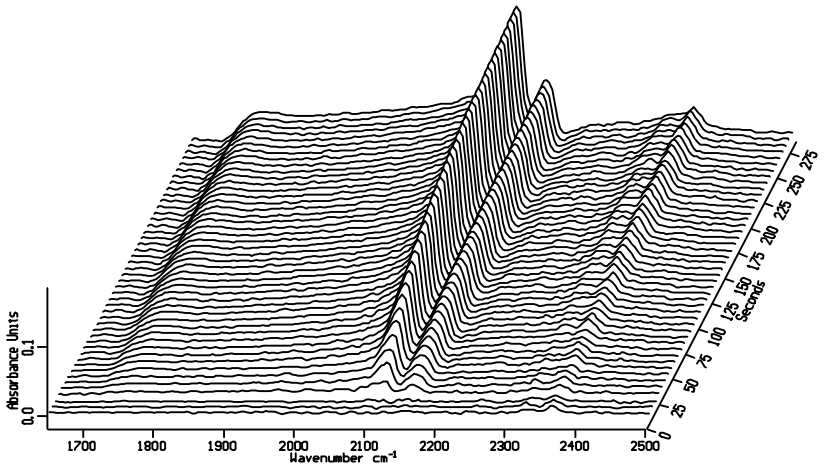

Figure 1. Typical FT-IR spectrum of a DNQ/novolac resist showing the change in the absorbance at ~2100 cm^{-1} as a function of exposure time. Illumination was with the white light illuminator of the microscope and is given in seconds. The scale is adjusted for clarity to show the absolute value of the change in absorbance. During exposure the absorbance between 2045 and 2206 cm^{-1} decreases, reflecting a decrease in DNQ concentration.

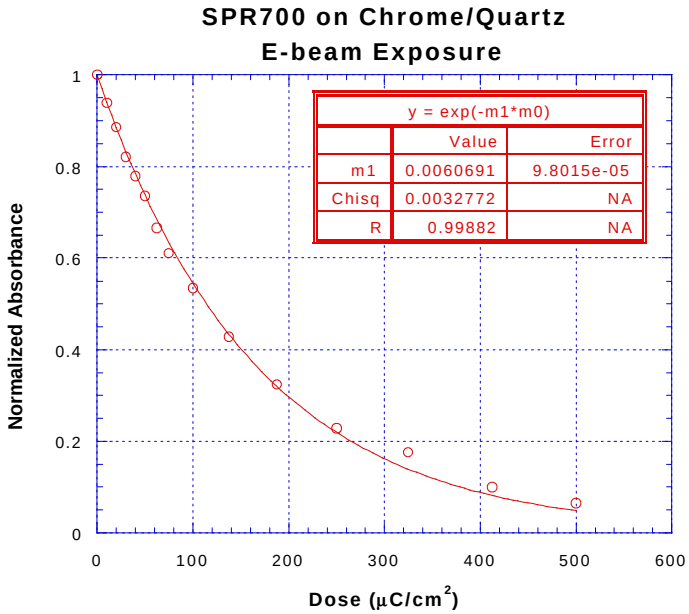

Figure 2. Determining the Dill C parameter for SPR700 on a chrome coated silicon dioxide substrate by plotting the normalized DNQ absorbance as a function of 50 kV e-beam exposure dose and obtaining the fit to the equation $m = e^{-CE}$.

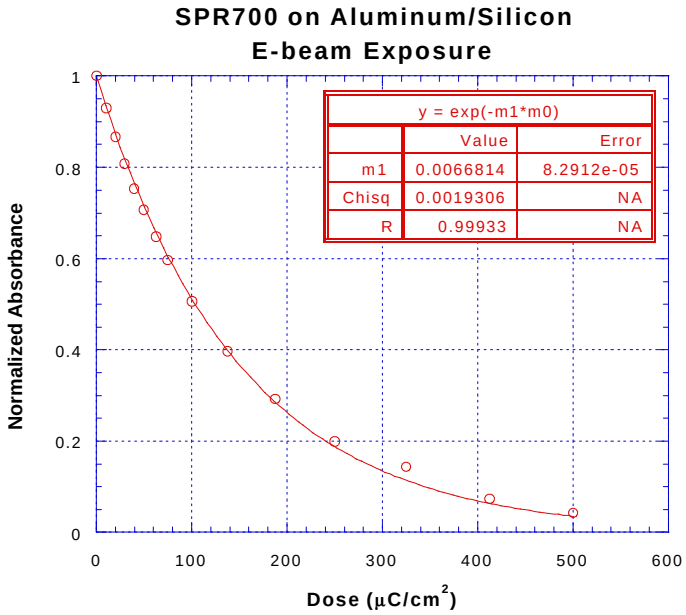

Figure 3. Determining the Dill C parameter for SPR700 on an aluminum coated silicon substrate by plotting the normalized DNQ absorbance as a function of 50 kV e-beam exposure dose and obtaining the fit to the equation $m = e^{-CE}$.

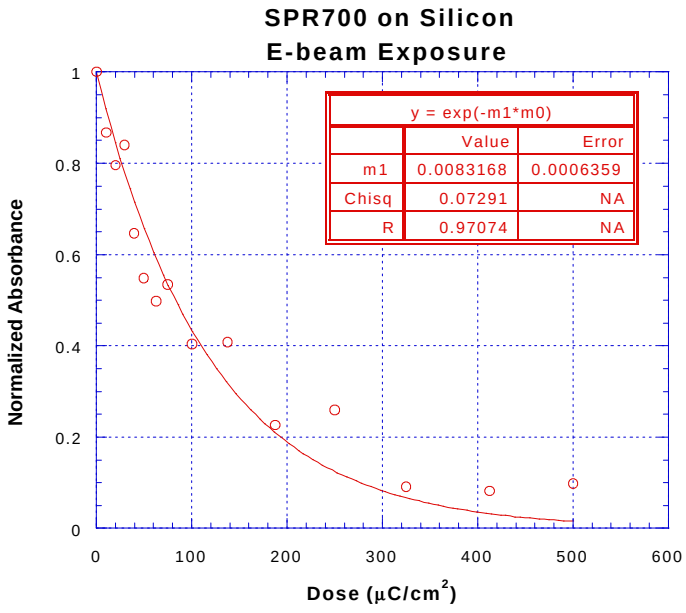

Figure 4. Determining the Dill C parameter for SPR700 on a silicon substrate by plotting the normalized DNQ absorbance as a function of 50 kV e-beam exposure dose and obtaining the fit to the equation $m = e^{-CE}$.

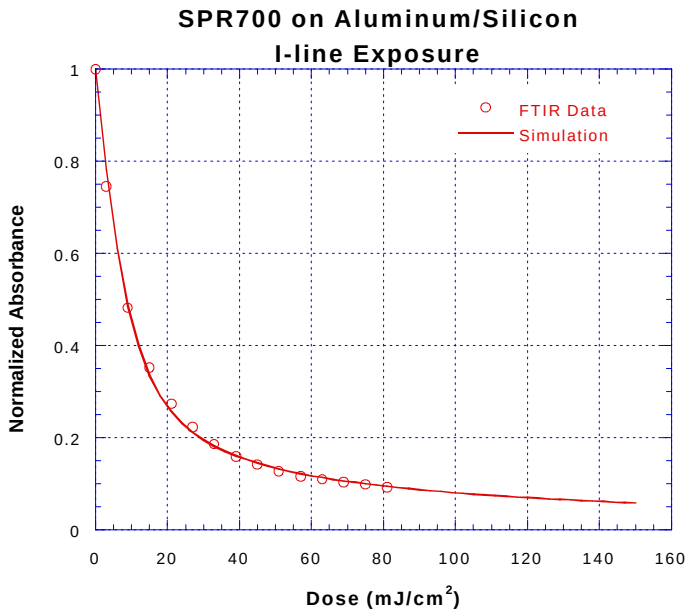

Figure 5. Determining the Dill C parameter for SPR700 on an aluminum coated silicon substrate by plotting the normalized DNQ absorbance as a function of i-line exposure dose and obtaining the fit to the data using ProABC.