Release Notes xxxx-xx-xx : : not ready at all My algrebra is really bad have some code to check however. **This is a draft and has not been peer reviewed or completely proof read but released in some state where it seems worthwhile given time or other constraints. Typographical errors are quite likely particularly in manually entered numbers. This work may include output from software which has not been fully debugged. For information only, not for use for any particular purpose see fuller disclaimers in the text. Caveat Emptor. This document is a non-public DRAFT and contents may be speculative or undocumented or simple musings and should be read as such.**

EUV Lithography : Don't take my kodachrome away

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EUV lithography appears to be optimal for just about everything to go wrong. The appeal of high resultion from the short wavelengths has been difficult to realize for economical production of complicated integrated circuits. Nominally "linear" real space imaging ignores a large number of easy ways to improve patterning using a photoresist with multi-photon dynamics. While this term seems to be associated with virtual intermediate states, it has been used to describe silver halide mechanisms , with long lived real states, for decades. A number of systems exist for things like photon up-conversion for example [19]. This work first reviews some simply possible multi-photon processes and their characteristic or D-log-E curves. One objectives is to get binary images with good latitude and this curve helps define that property. Another concern with EUV is the light quantization, often refered to as "stochastics' that cause fluctuations in exposure and noise in the developed pattern. A brief consideration of multi-photon effects on fluctuations and resolution is included. Much of this work is on the properties of silver halides that may be useful in an EUV resist but its worth nothing that some properties are also central to things like battery design. Besides the multi-photon resist specific additional areas are noted for further consideration. Inclusion of a mobile nucleus to form developable clusters for example. In the near death experience that is EUV litho, "move towards the light" seems apropos lol. The grains common in silver halide films are too coarse for nm scale patterning but the concept of a pixelated resist, with nm size squares devloping all-or-nothing, may be useful to consider further.

CONTENTS

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I. INTRODUCTION

EUV lithography is complicated by a number of issues with the photon energy and consequent physics and chemistry. At 13.5nm, the photon energy of 92 eV is well above chemical reaction thresholds and single absorption event generates an electron and hole cloud as the initial hot carriers thermalize. With typical exposure doses of 1mJ/cm2, this translates into only .7photos/nm2 but this is an average with fluctuations described by Poisson statistics for an uncorrelated light source. In the literature this quantization issue is often described as "stochastics." [8]a [30] The electron cloud may include emission into the vacuum and there is also residual gas excited by photons and secondary electrons to consider. As far as the chemistry goes, common organic photoresists will produce vapors that are as bad as any contaminant complicating EUV optical systems.

One important manifestations of the quantization of stochastics issue is "line edge roughness" (LER). This has been discussed in many ways including gross measures such as standard deviation or in more details exploring the frequency distribution of lithography and etch properties [29]. One focus of this work on multi-photon processes concerns a curve derived from uniform illumination which may seem irrelevant to idealized step desired in a final device structure at an edge. However, in real life illumination patterns have significant transition regions and if the curves are not step functions with light dose then there can be noise in the intermediate cases.

The focus of this work is on multi-photon processes for better use of the highly quantized light. Existing literature labelled as multi-photon for lithography apparently is specialized to high intensity lasers pumping into virtual states requiring simultaneous photons and therefore a high flux that is usually direct write scanned rather than masked [54] [40] [15] . The latter reference [15] discusses some multi-photon resist systems designed for maskless lithography and the achievement of sub-diffration $\lambda/14.8$ critical dimension although some of these concept may already be implemented in multi-trigger resists designed for masked (achieveable flux density) EUV lithoggrapy. Recently however some work has noted the problem suggesitng the use of real, long lived states and mentioning litrhography as a potential application [49] .

The mechanisms described here are most closely related to multi-trigger resists. In reality the reactions will be related to carriers more directly than photons and the terminology is a bit moot.

Multi-photon processes have been recognized for a long time as a way to improve resolution beyond what may be achievable from linear processes at a given wavelength. Significant detailed works exist on rate equations and interaction of the different processes that can occur.

In the EUV, control of fluctuations has been recognized as another important benefit and the literature on multi-trigger resists addresses this.

As no immediate solution appears to be completely supoerioer to the others or entirely satisfactory, this work goes through the rate equations for simplistic model equations motivating what may be expected from candidate systems.

Among the resist chemistries explored, metal oxides have been considered. However, there does not appear to be any serious consideration of the well known silver halide chemistry. This historical system is considered to illustrate some issues although it may not be adaptible to EUV. Silver halides, despite their wide range of apliations, do not appear to have much usage in the nm resolution range with ultra-fine grain dimensions being in the 35-50 nm range [23]. However, the goal of this work is to look at the mechanisms and determine if any of these are worth consideration for a possible new design.

Resists, like film, can be characterized by a curve relating exposure conditions to ultimate result after developing. Film often used the "D-log-E" curve relating the optical density of the final result to the integrated light dose at any point. Resists may be evaluated with many such functions such as thickness versus total energy dose (usually mJ/cm2). This work will consider generic rate equations initially and use terms like "D-log-E" as a generic or non-specific term for characteristic curve. In many imaging applications, linearity is desired. This is most easily achieved with one photon processes. In the case of lithography with a binary outcome, a sharp high-contrast sigmoidal curve is usually beneficial. Or as it has been said, " Higher contrasts lead to higher resolution in general and the resolution is the Holy Grail of microlithography" [17].

The intial discussion will try to find systems that generate sharp high contrast D-log-E curves wihle making best use of limited light and avoiding noise due to fluctuations.

The term sensitometric curve has also been used [53].

Contrast curve along with the term gamma for the slope in the transition region may also be used [17].

II. SOME MULTI-PHOTON BASICS

While the goal of lithography is high resolution low noise pattern transfer, the initial analysis of the multi-photon processes concerns uniform illumination to produce a binary outcome. First, the probability of success or failure, in essence development or non-development of a given image feature, is examined as a function of the expected number

of photons doses on that feature using just the Poisson distribtion. Then, some candidate chemical schemes are analyzed for their response curves and how they relate to imaging performance. Overall the goal is to find a system that generates high contrast with a minimum amount of light while providing low noise patterns and ideally having other features such as safe and cheap chemical implementations. With high resolution patterning, even in the EUV, diffration or other optical issues will create edge profiles that deviate from perfect step functions. The part of this illumination profile in the ambiguous region of the transfer curve, where success or failure is not assured, will create noise or uncertain results. So one goal is to make the characteristic or exposure curve as step-like or sigmoidal as limiting by realizable chemical systems and light budget.

II.1. Probability of success when n-photons needed

The starting point for probability of success or failure when n indepenent events are required for success is the Poisson Distribution which is introduced in many optics and statistics textbooks.

Thinking outloud
While not likely to be a source of confusion for this audience, its intersting to note the Poisson Effect may contributing to the competing approach of imprint lithography [22]

Its worth noting immediately that since we seek a solution and not just an exercise, that deviations from independene routinely occur due to the nature of a light source or electrons in the case of photon and electron counting [44] [2] both of which may be relevant in formulating a good solution for high-contrast imaging. Interesting phenomena occur, for example, in lasers [46] and photolelectron statistics [32] among others.

In this case we will consider the probability of getting n or fewer photons (or electrons or whatever) as a function of an expected number $< n >$. The probability of getting n_t or fewer things with $< n >$ is

$$P(n <= n_t; < n >) = \sum_{k=0}^{n_t} \frac{< n >^k}{k!} exp(- < n >) \tag{1}$$

Thinking outloud
its interesting to note, surprising but of unknown significance, in passing that there is always a higher probability of getting an even number of photons

$$P_{even} = \sum \frac{< n >^{2k})}{(2k)!} exp(- < n >) = cosh(< n >) exp(- < n >) = \frac{1 + exp(-2 < n >)}{2} \tag{2}$$

although the opposite is the case of zero is excluded.

This simple sum Eqn 1 is a truncated taylor series for exp(x) timex exp(-x).

These sums will be used as non-exposure curves versus light dose or $< n >$ (interchangeably with their complementary exposure curves). In lithography a binary high-constrast image is desired which is opposite of what may be desired in other imaging applications where linearlity and high dynamic range matter. Getting a sigmoidal rather than a linear curve early in the processing may have some benefits over thresholding later with a deverloper process.

Important features include the number of zero derivatives at the origin and range of "confusion" where sucess probability is not near zero or one. The general form of this sum is

$$S = P(x) exp(-x) \tag{3}$$

and its easy to show that

$$\frac{d^m S}{dx^m} = exp(-x)(D-1)^m P(x) \tag{4}$$

where D is the derivative operator . More specialized to the current situation, the first 2 derivatives are

$$\frac{dP(n <= n_t; < n >)}{d < n >} = -\frac{< n >^{n_t}}{n_t!} exp(- < n >) \tag{5}$$

and

$$\frac{d^2P(n <= n_t; < n >)}{d < n >^2} = -\frac{< n >^{(n_t-1)}}{(n_t-1)!}\left(1 - \frac{< n >}{n_t}\right) exp(- < n >) \tag{6}$$

with the latter going to zero at $n_t =< n >$ giving the maximum derivative as

$$max(-\frac{dP(n <= n_t; < n >)}{d < n >}) = \frac{n_t^{n_t}}{n_t!} exp(-n_t) \tag{7}$$

which brings to mind Stirling's approximation,

$$n_t! \approx \sqrt{2\pi n_t} {n_t}^{n_t} e^{-n_t} \tag{8}$$

$$max(-\frac{dP(n <= n_t; < n >)}{d < n >}) \approx \frac{1}{\sqrt{2\pi n_t}} \tag{9}$$

D_{max} seems to decrease with n_t,

$$\frac{max(-d_{n+1})}{max(-d_n)} = exp(-1)\left(\frac{n+1}{n}\right)^n \approx .368\left(\frac{n+1}{n}\right)^n \tag{10}$$

noting that

$$lim_{n\to\infty}\left(\frac{n+1}{n}\right)^n = e \tag{11}$$

this goes to 1 for large n. Similarly using Eqn 9,

$$\frac{max(-d_{n+1})}{max(-d_n)} \approx \frac{\sqrt{n_t}}{\sqrt{n_t+1}} \tag{12}$$

Thinking outloud

Properies of the n-photon sums								
n_t	n-needed	m - mid =5	n-p=.1	n -p =.9	range	range/n-ph	max d/dn	p at max d/dn
0	1	0.693	2.3	0.105	2.2	2.2	-1	1
1	2	1.68	3.89	0.532	3.36	1.68	-0.368	0.736
2	3	2.67	5.32	1.1	4.22	1.41	-0.271	0.677
3	4	3.67	6.68	1.74	4.94	1.23	-0.224	0.647
4	5	4.67	7.99	2.43	5.56	1.11	-0.195	0.629
5	6	5.67	9.27	3.15	6.12	1.02	-0.175	0.616
6	7	6.67	10.5	3.89	6.64	0.948	-0.161	0.606
7	8	7.67	11.8	4.66	7.11	0.889	-0.149	0.599
8	9	8.67	13	5.43	7.56	0.84	-0.14	0.593
9	10	9.67	14.2	6.22	7.98	0.798	-0.132	0.587
10	11	10.7	15.4	7.02	8.39	0.762	-0.125	0.583
11	12	11.7	16.6	7.83	8.77	0.731	-0.119	0.579
12	13	12.7	17.8	8.65	9.14	0.703	-0.114	0.576
13	14	13.7	19	9.47	9.49	0.678	-0.11	0.573
14	15	14.7	20.1	10.3	9.83	0.655	-0.106	0.57
15	16	15.7	21.3	11.1	10.2	0.635	-0.102	0.568
16	17	16.7	22.5	12	10.5	0.616	-0.0992	0.566
17	18	17.7	23.6	12.8	10.8	0.599	-0.0963	0.564
18	19	18.7	24.8	13.7	11.1	0.583	-0.0936	0.562
19	20	19.7	25.9	14.5	11.4	0.569	-0.0911	0.561
20	21	20.7	27	15.4	11.7	0.555	-0.0888	0.559
97	98	97.7	111	85.5	25.3	0.259	-0.0405	0.527
98	99	98.7	112	86.5	25.5	0.257	-0.0403	0.527
99	100	99.7	113	87.4	25.6	0.256	-0.0401	0.527
100	101	101	114	88.4	25.7	0.255	-0.0399	0.527
101	102	102	115	89.3	25.8	0.253	-0.0397	0.526
996	997	997	1.02e+03	957	67.2	0.0674	-0.0126	0.508
997	998	998	1.02e+03	958	66.3	0.0664	-0.0126	0.508
998	999	999	1.02e+03	959	65.3	0.0654	-0.0126	0.508
999	1000	1e+03	1.02e+03	960	64.3	0.0643	-0.0126	0.508
1000	1001	1e+03	1.02e+03	961	63.3	0.0633	-0.0126	0.508
1001	1002	1e+03	1.02e+03	962	62.3	0.0622	-0.0126	0.508

TABLE I. Tables may be old fashion but may be useful for reference here. The values include n_t or upper sum limit, n the number of photons needed for success, the value of $< n >$ for P=.5,.1, and .9 to define the region of confusion and finally the maximum slope and its location p. ./mjm_poisson.out -cmd "table nmax=20;v0=.1;v1=.9;write_lbl=0;prec=3" quit

Some of these results are tabulated in Table I to illustrate trends and tradeoffs. As the number of photons is increased, more of course are needed to get a response with good probability but the range of confusion where unpredictable results would be produced slowly shrinks as a percentage of the photon dose.

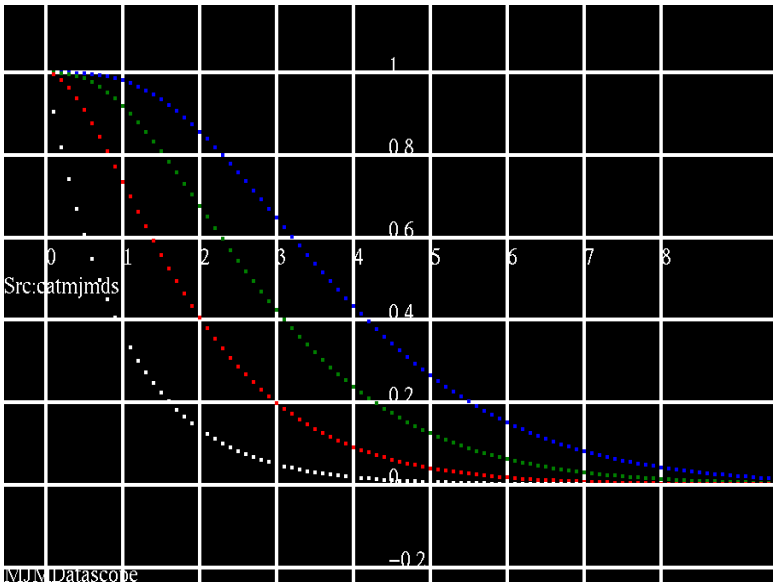


FIG. 1. Multiphoton probability of failure curves for 1,2,3, and 4 photon processes . plotsome2.txt

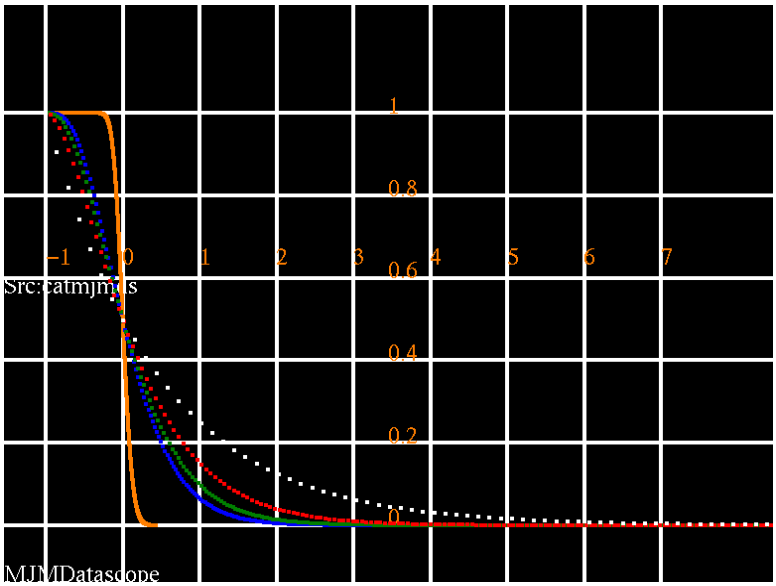


FIG. 2. Multiphoton scaled and translated to intersect at .5 . Illustrated are 1,2,3,4, and 101 photon curves. plotsome.txt

III. BASIC MULTI-PHOTON SYSTEMS AND THEIR CURVES

Various exposure curves can be implemented in hypothetical normalized systems as shown here. This topic includes a comparison of systems with real and virtual intermediate states which has been discussed in more detail in contemporary works looking at multiphoton system measurement [31] for example.

This analysis relates to the idea expressed in Fukuda in 2025 [12] that part of the problem with EUV vs DUV is in the resist dealing with image contrast. Other issues are moved from developer chemistry to earlier photocarrier involved reactions although the author does go on to explain how effecitvely multi-photons are required anyway for development.

A simple n-photon system can repdouce the curves from the prior section but more complicated or modified real systems may be more difficult to analyze. In the following a constant light flux, ϕ, illuminates a variety of chemical species denoted by capital letters. Arbitrary constants are included only to illustrate specific issues. While encountered in real implementations, they may obscure the initial dynamics. Note too that some cases such as very high photon

number may not be realizable with any practical or known system but illustrate potential benefits if such a system could be created.

III.1. Cascade or Ladder

This is the "pure" multi-photon system where a developer responds to some species which requires n photons to synthesize.

Consider a cascade or ladder or serial processes such that $X_i + h\nu \longrightarrow X_{i+1}$

for i=0 to i=n-1. The rate equations then are

$$\frac{dX_i}{dt} = c\phi X_{i-1} - c\phi X_i \tag{13}$$

and for i==0,

$$X_0(t) = X_0(0)exp(-c\phi t) \tag{14}$$

and for i==n,

$$\frac{dX_n}{dt} = c\phi X_{i-1} \tag{15}$$

Successively integrating gives,

$$X_{i+1}(t) = X_i(0)\frac{(c\phi t)^(i+1)}{(i+1)!}exp(-c\phi t) \tag{16}$$

except at the ends points. X_0 was already given and X_n lacking the photoconversion to another species gives

$$X_n = X_0(0)(1 - \exp(-c\phi t)\sum_0^{n-1}\frac{(c\phi t)^i}{i!}) \tag{17}$$

$$X_n/X_0(0) = 1 - \exp(-c\phi t)\sum_0^{n-1}\frac{(c\phi t)^i}{i!} \tag{18}$$

which is exactly the (complement of the) Poisson probability of exposure Eqn 1 with $< n >= c\phi t$ and $n_t = n - 1$ the most number of photons that fail to create a developable feature.

III.2. Cascade or Ladder with Finite Lifetime States

The above specialized case reproducted the Poisson probability of failure and is a good limiting case for further work. Before getting to the system normally called multi-photon in which all photons are absorbed simultaneously, it may be usful to look at the case of a finite lifetime intermediate state or a leaky integrator of photon flux.

The general system is,

$$X_0 + h\nu \longrightarrow X_1$$
$$X_{i-1} + h\nu \longrightarrow X_i$$
for i not equal zero or n,
$$X_i \xrightarrow{k} X_{i-1}$$

$$\frac{dX_i}{dt} = -\phi X_i + \phi X_{i-1} + kX_{i+1} - kX_i \tag{19}$$

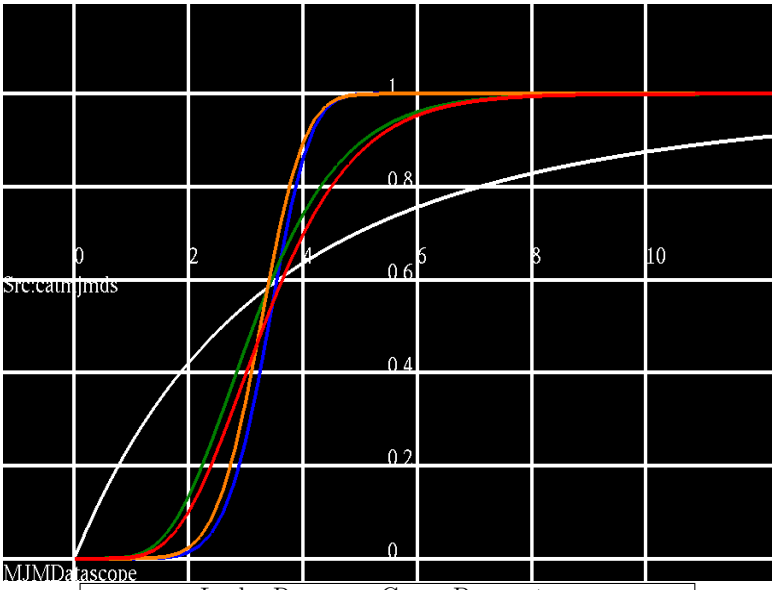
otherwise with no decay from terminal state,

$$\frac{dX_n}{dt} = \phi X_{n-1} \tag{20}$$

$$\frac{dX_{n-1}}{dt} = -\phi X_{n-1} + \phi X_{n-2} - kX_n - 1 \tag{21}$$

$$\frac{dX_0}{dt} = -\phi X_0 + kX_1 \tag{22}$$

FIG. 3. Leaking integrators with loss finite lifetime states but stable terminal state .



Leaky Response Curve Parameters						
color	n-species	k	exp time	phi-10	phi-50	phi-90
white	2	-	.3	0.358753	2.59927	11.5451
green	10	0	2.75	1.85584	3.13446	5.05911
red	10	.5	3	2.00123	3.31509	5.24203
orange	10	5	50	2.4503	3.25675	4.02285
blue	10	6	100	2.6079	3.39818	4.11833

FIG. 4. Some exposure curves demonstrating less confusion with the loss terms. The y-axis is P of developing while the X-axis is photon flux with exposure time adjusted to get overlapping curves. The exposure time ratio is 333 between 1 photon and the very lossy case. Note that the values here for illustration and may not reflect typial realizable systems of interest ./plotleak

If this seems familiar its redundant with preceding section in mjm_euv_multi.tex. However, the terms are grouped differently to show tri-diagonal structure and detail the corner cases for small n. I wrote "mjm_math" to do a few polynomial manipulations although it could probably be done in a variety of existing things like mathematica or sympy.

$$\mathrm{X_0} + \mathrm{h}\nu \longrightarrow \mathrm{X_1}$$
$$\mathrm{X_{i\text{-}1}} + \mathrm{h}\nu \longrightarrow \mathrm{X_i}$$
for i not equal zero or n,
$$\mathrm{X_i} \xrightarrow{k} \mathrm{X_{i\text{-}1}}$$

$$\frac{dX_i}{dt} = -\phi X_i + \phi X_{i-1} + kX_{i+1} - kX_i = \phi X_{i-1} - (\phi + k)X_i + kX_{i+1} \tag{23}$$

otherwise with no decay from terminal state,

$$\frac{dX_n}{dt} = \phi X_{n-1} \tag{24}$$

$$\frac{dX_{n-1}}{dt} = -(\phi + k)X_{n-1} + \phi X_{n-2} \tag{25}$$

$$\frac{dX_0}{dt} = -\phi X_0 + kX_1 \tag{26}$$

FIG. 5. With loss finite lifetime states but stable terminal state .

Thinking outloud
wtf n=2,

$$\frac{d^2X_2}{dt^2} = \phi\frac{dX_1}{dt} \tag{27}$$

$$\frac{d^2X_2}{dt^2} = \left(-(\phi+k)\phi X_1 + \phi^2 X_0\right) \tag{28}$$

$$\frac{d^2X_2}{dt^2} = \left(-(\phi+k)\frac{dX_2}{dt} + \phi^2 X_0\right) \tag{29}$$

$$\frac{d^2X_2}{dt^2} + (\phi+k)\frac{dX_2}{dt} = \phi^2 X_0 \tag{30}$$

$$\frac{d^3X_2}{dt^3} + (\phi+k)\frac{d^2X_2}{dt^2} = \phi^2\frac{dX_0}{dt} \tag{31}$$

$$\frac{d^3X_2}{dt^3} + (\phi+k)\frac{d^2X_2}{dt^2} = \phi^2\left(-\phi X_0 + kX_1\right) \tag{32}$$

$$\frac{d^3X_2}{dt^3} + (\phi+k)\frac{d^2X_2}{dt^2} = -\phi^3 X_0 + k\phi\frac{dX_2}{dt} \tag{33}$$

$$\frac{d^3X_2}{dt^3} + (\phi+k)\frac{d^2X_2}{dt^2} - k\phi\frac{dX_2}{dt} = -\phi^3 X_0 \tag{34}$$

$$\frac{d^3X_2}{dt^3} + (\phi+k)\frac{d^2X_2}{dt^2} - k\phi\frac{dX_2}{dt} = -\phi\left(\frac{d^2X_2}{dt^2} + (\phi+k)\frac{dX_2}{dt}\right) \tag{35}$$

$$\frac{d^3X_2}{dt^3} + (2*\phi+k)\frac{d^2X_2}{dt^2} + \phi^2\frac{dX_2}{dt} = 0 \tag{36}$$

$$r(r^2 + (2\phi+k)r + \phi^2) = 0 \tag{37}$$

$$b^2 = 4\phi^2 + k^2 + 4k\phi \tag{38}$$

$$b^2 - 4ac = k^2 + 4k\phi \tag{39}$$

$$r = -\phi - \frac{k}{2} \pm \sqrt{k(k+4\phi)} \tag{40}$$

Thinking outloud
n=3,

$$\frac{dX_3}{dt} = \phi X_2 \tag{41}$$

$$\frac{dX_2}{dt} = -(\phi + k)X_2 + \phi X_1 \tag{42}$$

$$\frac{dX_1}{dt} = -(\phi + k)X_1 + \phi X_0 - kX_2 \tag{43}$$

$$\frac{dX_0}{dt} = -\phi X_0 + kX_1 \tag{44}$$

$$\frac{d^2X_3}{dt^2} = \phi \frac{dX_2}{dt} \tag{45}$$

$$\frac{d^2X_3}{dt^2} = \left(-(\phi + k)\phi X_2 + \phi^2 X_1\right) \tag{46}$$

$$\frac{d^2X_2}{dt^2} = \left(-(\phi + k)\frac{dX_3}{dt} + \phi^2 X_1\right) \tag{47}$$

$$\frac{d^2X_3}{dt^2} + (\phi + k)\frac{dX_3}{dt} = \phi^2 X_1 \tag{48}$$

$$\frac{d^3X_3}{dt^3} + (\phi + k)\frac{d^2X_3}{dt^2} = \phi^2 \frac{dX_1}{dt} \tag{49}$$

$$\frac{d^3X_3}{dt^3} + (\phi + k)\frac{d^2X_3}{dt^2} = \phi^2 \left(-(\phi + k)X_1 + \phi X_0 - kX_2\right) \tag{50}$$

$$\frac{d^3X_3}{dt^3} + (\phi + k)\frac{d^2X_3}{dt^2} = -(\phi + k)(\frac{d^2X_3}{dt^2} + (\phi + k)\frac{dX_3}{dt}) + \phi^3 X_0 - k\phi\frac{dX_3}{dt} \tag{51}$$

$$\frac{d^3X_3}{dt^3} + 2(\phi + k)\frac{d^2X_3}{dt^2} + ((\phi + k)^2 + k\phi)\frac{dX_3}{dt}) = \phi^3 X_0 \tag{52}$$

$$\frac{d^4X_3}{dt^4} + 2(\phi + k)\frac{d^3X_3}{dt^3} + ((\phi + k)^2 + k\phi)\frac{d^2X_3}{dt^2}) = -\phi^4 X_0 + k\phi^3 X_1 \tag{53}$$

Thinking outloud
n==3 part 2
repeat,

$$\frac{d^4X_3}{dt^4} + 2(\phi+k)\frac{d^3X_3}{dt^3} + ((\phi+k)^2 + k\phi)\frac{d^2X_3}{dt^2}) = -\phi^4 X_0 + k\phi^3 X_1 \tag{54}$$

use identities,

$$\frac{d^3X_3}{dt^3} + 2(\phi+k)\frac{d^2X_3}{dt^2} + ((\phi+k)^2 + k\phi)\frac{dX_3}{dt}) = \phi^3 X_0 \tag{55}$$

$$\frac{d^3X_3}{dt^3} + (\phi+k)\frac{d^2X_3}{dt^2} = \phi^2\frac{dX_1}{dt} \tag{56}$$

$$\frac{d^2X_3}{dt^2} + (\phi+k)\frac{dX_3}{dt} = \phi^2 X_1 \tag{57}$$

$$\frac{d^4X_3}{dt^4}+2(\phi+k)\frac{d^3X_3}{dt^3}+((\phi+k)^2+k\phi)\frac{d^2X_3}{dt^2}) = -\phi\frac{d^3X_3}{dt^3}-\phi 2(\phi+k)\frac{d^2X_3}{dt^2}-\phi((\phi+k)^2+k\phi)\frac{dX_3}{dt})+k\phi\frac{d^2X_3}{dt^2}+k\phi(\phi+k)\frac{dX_3}{dt} \tag{58}$$

$$\frac{d^4X_3}{dt^4} + (3\phi+2k)\frac{d^3X_3}{dt^3} + ((\phi+k)^2 + 2k\phi + 2\phi^2)\frac{d^2X_3}{dt^2} + \phi((\phi+k)^2 - k*k)\frac{dX_3}{dt} = 0 \tag{59}$$

$$\frac{d^4X_3}{dt^4} + (3\phi+2k)\frac{d^3X_3}{dt^3} + (k^2 + 4k\phi + 3\phi^2)\frac{d^2X_3}{dt^2} + (\phi^3 + 2k\phi^2)\frac{dX_3}{dt} = 0 \tag{60}$$

The characteristic equation then is,

$$\frac{d^2X_n}{dt^2} = \phi\frac{dX_{n-1}}{dt} \tag{61}$$

$$\frac{d^2X_n}{dt^2} = \phi\left(-(\phi+k)\frac{dX_{n-1}}{dt} + \phi\frac{dX_{n-2}}{dt}\right) \tag{62}$$

$$\frac{d^2X_n}{dt^2} = \phi\left(-(\phi+k)\frac{dX_n}{dt} + \phi\frac{dX_{n-2}}{dt}\right) \tag{63}$$

$$\frac{d^2X_n}{dt^2} = -(\phi+k)\phi\frac{dX_n}{dt} + \phi^2\frac{dX_{n-2}}{dt} \tag{64}$$

$$\frac{d^2X_n}{dt^2} + (\phi+k)\phi\frac{dX_n}{dt} = \phi^2\frac{dX_{n-2}}{dt} \tag{65}$$

For n=2,

$$\frac{d^2X_2}{dt^2} + (\phi+k)\phi\frac{dX_2}{dt} = \phi^2\left(-\phi X_0 + kX_1\right) = -\phi^3 X_0 + k\phi\frac{dX_2}{dt} \tag{66}$$

$$\frac{d^2X_2}{dt^2} + \phi^2\frac{dX_2}{dt} = -\phi^3 X_0 \tag{67}$$

$$\frac{d^3X_2}{dt^3} + \phi^2\frac{d^2X_2}{dt^2} = -\phi^3\frac{dX_0}{dt} = \phi^4 X_0 - \phi^3 k X_1 \tag{68}$$

$$\frac{d^3X_2}{dt^3} + \phi^2\frac{d^2X_2}{dt^2} = -\phi^3\frac{dX_0}{dt} = -\phi\frac{d^2X_2}{dt^2} - \phi^3\frac{dX_2}{dt} - \phi^3 k X_1 \tag{69}$$

$$\frac{d^3X_2}{dt^3} + (\phi^2+\phi)\frac{d^2X_2}{dt^2} + \phi^3\frac{dX_2}{dt} = -\phi^3 k X_1 = -\phi^2 k\frac{dX_2}{dt} \tag{70}$$

$$\frac{d^3X_2}{dt^3} + (\phi^2+\phi)\frac{d^2X_2}{dt^2} + (\phi^3+\phi^2 k)\frac{dX_2}{dt} = 0 \tag{71}$$

$$r(r^2 + r(\phi+\phi^2) + \phi^2(\phi+k)) = 0 \tag{72}$$

$$b^2 = \phi^2(1 + 2\phi + \phi^2) \tag{73}$$

$$b^2 - 4ac = \phi^2(1 + 2\phi + \phi^2) - 4 * \phi^2(\phi + k) \tag{74}$$

The silver halids and probably other systems will have more paramter variation and more physical effects making the equations more complicated. With computers and numerical codes it may not seem worthwhile to explore these analytically but they are useful for early thinking about candidate photo systems.

In a simple 2 photon process a light flux ϕ converts A into B and a potentially different flux or different rate, ψ, converts B into C. B can also decay back to A.

$$\begin{gathered} \mathrm{A} + \mathrm{h}\nu \longrightarrow \mathrm{B} \\ \mathrm{B} + \mathrm{h}\nu_2 \longrightarrow \mathrm{C} \\ \mathrm{B} \xrightarrow{k_1} \mathrm{A} \end{gathered}$$

$$\frac{dA}{dt} = -\phi A + k_1 B \tag{75}$$

$$\frac{dB}{dt} = \phi A - k_1 B - \psi B \tag{76}$$

$$\frac{dC}{dt} = \psi B \tag{77}$$

FIG. 6. With loss of unstable intermediate B

As before variables can be eliminated and a single higher order linear equation can be solved.

Show Work characteristic eqn

$$\frac{d^2A}{dt^2} = -\phi\frac{dA}{dt} + k_1\frac{dB}{dt} \tag{78}$$

$$\frac{1}{k_1}(\frac{d^2A}{dt^2} + \phi\frac{dA}{dt}) = \frac{dB}{dt} \tag{79}$$

$$\frac{1}{k_1}(\frac{dA}{dt} + \phi A) = B \tag{80}$$

$$\frac{dB}{dt} = \phi A - k_1 B - \psi B = \phi A - (k_1 + \psi)B \tag{81}$$

$$\frac{1}{k_1}(\frac{d^2A}{dt^2} + \phi\frac{dA}{dt}) = \phi A - k_1 B - \psi B = \phi A - (k_1 + \psi)(\frac{1}{k_1}(\frac{dA}{dt} + \phi A)) \tag{82}$$

$$\frac{1}{k_1}(\frac{d^2A}{dt^2} + \phi\frac{dA}{dt}) = \phi A - (k_1 + \psi)(\frac{1}{k_1}(\frac{dA}{dt} + \phi A)) \tag{83}$$

$$\frac{1}{k_1}\frac{d^2A}{dt^2} + \frac{1}{k_1}\phi\frac{dA}{dt} = (\phi - \frac{\psi\phi}{k_1} - \phi)A - (k_1 + \psi)\frac{1}{k_1}\frac{dA}{dt} \tag{84}$$

$$\frac{1}{k_1}\frac{d^2A}{dt^2} + (k_1 + \psi + \phi)\frac{1}{k_1}\frac{dA}{dt} + \frac{\phi\psi}{k_1}A = 0 \tag{85}$$

$$\frac{d^2A}{dt^2} + (k_1 + \psi + \phi)\frac{dA}{dt} + \phi\psi A = 0 \tag{86}$$

$$r = -\frac{(k_1 + \psi + \phi)}{2} \pm \frac{1}{2}\sqrt{(k_1 + \psi + \phi)^2 - 4\phi\psi} \tag{87}$$

$$r = -\frac{(k_1 + \psi + \phi)}{2} \pm \frac{1}{2}\sqrt{k_1^2 + 2k_1 * (\phi + \psi) + (\psi + \phi)^2 - 4\phi\psi} \tag{88}$$

$$r = -\frac{(k_1 + \psi + \phi)}{2} \pm \frac{1}{2}\sqrt{k_1^2 + 2k_1 * (\phi + \psi) + (\psi - \phi)^2} \tag{89}$$

Its probably worth nothing that the earlier system had degenerate roots and this one may approach that. Consider two roots r and $(r + \delta)$ and pairs of constants A_x and A_y defined below. In the limit of small δt the exponential can be expanded although for finite δ this will always grow with time.

Show Work degenerate roots

$$A = A_- e^{rt} + A_+ e^{(r+\delta)t}; \frac{dA}{dt} = A_- r e^{rt} + A_+(r + \delta)e^{(r+\delta)t} \tag{90}$$

$$A(0) = A_- + A_+; \frac{dA}{dt}(0) = A_- r + A_+(r + \delta) = -\phi A(0) \tag{91}$$

$$rA(0) + A_+\delta = -\phi A(0) \tag{92}$$

$$(\phi + r)A(0) = -A_+\delta \tag{93}$$

Using "engineering (aka gutter) math" take limit as delta goes to zero,

$$A = e^{rt}(A_z + A_d(1 + \delta t)) \tag{94}$$

; change variables,

The general solution can be written as,

$$A = e^{rt}(A_1 + A_2\delta t) \tag{95}$$

; with

$$\frac{dA}{dt} = e^{rt}(A_2\delta + rA_1 + rA_2\delta t) \tag{96}$$

; and its possible to solve for $A_2\delta$ product,

$$A(0) = A_1 \tag{97}$$

;

$$\frac{dA}{dt}(0) = (rA(0) + A_2\delta(1+0)) \tag{98}$$

;

$$A_2\delta = \frac{dA}{dt}(0) - rA(0) \tag{99}$$

; or

$$A = e^{rt}(A(0) + (\frac{dA}{dt}(0) - rA(0))t) \tag{100}$$

;

In any case the discriminant is positive semidefinite and an osillatory response is not possible.

III.3. Simultaneous Multi-photon Absorption

One point of this work is to use the multi-photon term for processes such as the above although in general usage for EUV it seems to be specialized to simulateous absorption of n-photons or proceeeding through virtual states. As shown in the previous section, the temporal correlation related to the leaky integration helps to sharpen the curve and in fact the simultaneous curve does appear to have a smaller zone of confusion than the long lived intemediate state case for same number of required photons but of course it wastes more.

$$\mathrm{A} + \mathrm{nh}\nu \longrightarrow \mathrm{B}$$

$$\frac{dA}{dt} = -A\phi^n \tag{101}$$

$$\frac{dB}{dt} = A\phi^n \tag{102}$$

$$A(t) = A(0)(exp(-\phi^n t)) \tag{103}$$

$$\frac{dB}{dt} = \phi^n A(0)(exp(-\phi^n t)) \tag{104}$$

$$B(t) = A(0)(1 - exp(-\phi^n t)) \tag{105}$$

$$B(\phi; t) = A(0)(1 - exp(-\phi^n t)) \tag{106}$$

versus

$$X_n = X_0(0)(1 - \exp(-\phi t)\sum_0^{n-1}\frac{(\phi t)^i}{i!}) \tag{107}$$

FIG. 7. Multiple photons per simultaneous reaction generate Eqn 106 versus Eqn 17 reproduced here as Eqn 107 without the constant.

Note that these are all exponential in time but for a given scene at fixed time the exposure curve $B(\phi)$ does become sigmoidal and

$$\frac{dB(\phi; t)}{d\phi} = tn\phi^{n-1}exp(-\phi^n t)) \tag{108}$$

with n-1 zero derivatives at zero light levels. With second derivative($n > 1$),

$$(-t^2n^2\phi^{2n-2} + tn(n-1)\phi^{n-2})exp(-\phi^n t)) \tag{109}$$

the maximum slope appears at

$$t = \frac{n-1}{n}\phi^{-n} \tag{110}$$

with value

$$\frac{dB(\phi;t)}{d\phi}_{max} = tn\phi^{n-1}exp(-\phi^n t)) = (n-1)\phi^{-1}exp(-\frac{n-1}{n})), n > 1 \tag{111}$$

Thinking outloud
check this lol

The $n = 1$ result does not seem right but the max is at $\phi = 0$,

$$\frac{dB(\phi;t)}{d\phi}_{max} = texp(-\phi t) = t \tag{112}$$

Comparing Eqn 106 to Eqn 17 or Eqn 107, the lack of time integration is obvious from the apprerance of t to first power only.

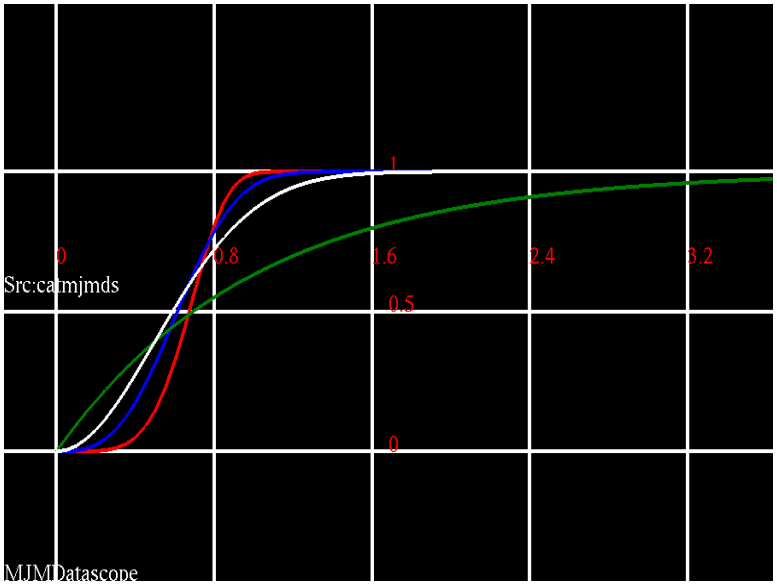


FIG. 8. Multi-photon simulatnaous for t=n=1(green),2(white),3(blue),and 5(red). Time was set equal to photon number to make curves overlap better to show relative shapes. ./plotsimul

III.4. Multi-step or maybe pyramind

A differnt example more similar to "multi-trigger" imaging gives the same result. Consider the system and rate equations in Fig. 9,
with initially A(0)=A_0 and B(0)=0.

$$A(t) = A(0)(exp(-\phi t)) \tag{116}$$

giving

$$\frac{dB}{dt} = \phi A(0)exp(-\phi t) - kB^n \tag{117}$$

With the developer responding to [C] the response curve does have n zero derivatives at the origin as B(0) is zero but the details are different. B responds more quickly as its first order but then there is a long tail in C as B is depleted. Changing k from unity can help. To modify this system to copy the Poisson n-photon results?

$$\mathrm{A} + \mathrm{h}\nu \longrightarrow \mathrm{B}$$
$$\mathrm{nB} \xrightarrow{k} \mathrm{C}$$

$$\frac{dA}{dt} = -A\phi \tag{113}$$

$$\frac{dB}{dt} = -\frac{dA}{dt} - \frac{dC}{dt} = A\phi - nkB^n \tag{114}$$

$$\frac{dC}{dt} = kB^n \tag{115}$$

FIG. 9. Multi-step or pyamid

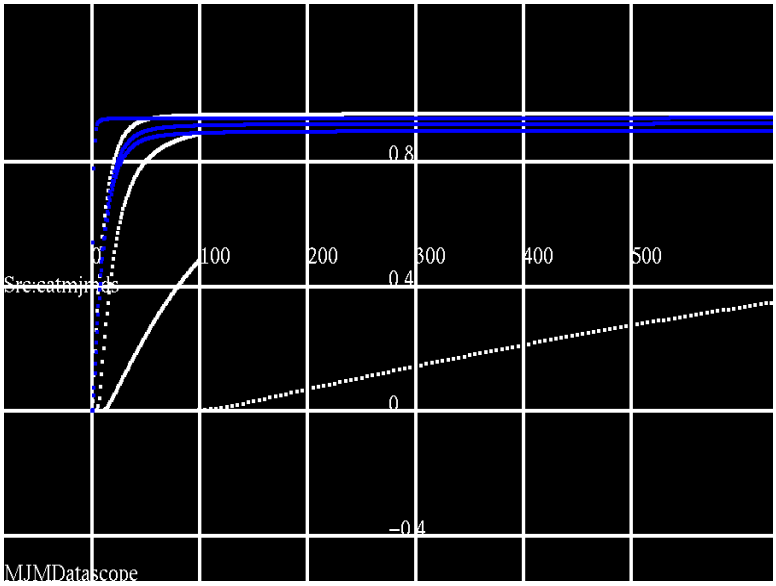


FIG. 10. Some miscellaneous pyramid transfer curves including some with decay of B back to A. The initial zero derivative could be demonstrated but the slope through transition region was comparatively low and asymptotes were usually less than 1. $./mjm_poisson.out"testtest = pyramid; n = 10; dt = .00001; time = .001; k = 100; phi = .0; dphi = 5; nphi = 1000; color = white; itaut = 100"quit$

The resolution and fluctuatin properties of multi-photon processes are also beneficial.

III.5. Some EUV Resists - CAR and MTR etc

III.5.1. Chemically Amplified

Several good reviews exist [17]. The important points which can be found detailed in most references relate to multiple chemical reactions in response to one photon. As usually used in the field, chemically amplified resists sense UV light with a photoacid generator(PAG) and use the generated acid to catalytically remove groups from a polymer. Polymers with enough removed groups are lost during development. PAG's appear to commonly use sulfur species. The "deprotection" scheme is common although polymerization and depolymerization are also possible.

A 2022 review compared some CAR's, MOR's, and MTR with an EUV interference grating illumination pattern demonstrating some benefits of the MTR method although all resits had some limitations [9]. Interfernce between plane waves would generate a sinusidal intensity profile and the resulting intensity profile is claimed as sinusoidal. In any case the line edges will not be digital or "sharp" and have some profile although in actual lithography this may be different and variable the resist with a high-contrast transfer function may have noise benefits. The spatial frequencies or other parameters of the noise may not be evident and problems like diffusion will not be considered but sharp transitions create a better starting point than exponential or gradual ones.

Attempts to optimize resist parameters for EUV have not always produced the expected results. A 2018 attempt to add proprietary Mg and related salts as sensitizers actually decreased EUV absorption and largely increased roughness while increasing acid generation and apparent electron generation [48]. The ability to change the electron-hole pair generation energy, usually estimated using Klein's 3x the bandgrap rule in semoconductors, creates some interesting possibilities although impoved photon efficiency would probably help quanizatin problems more.

More recently around the turn of the century, some benefits were observed with Sn in the right environment without amplification [3].

In the prior curves, "photon" was used as a generic term but in reality reactions could be initiated by electrons fron an initial absorption event or from the ambient. A background of ions may exist which could create a uniform fog or exposure and a multi-event resist may be able to avoid some of this pattern deterioration.

III.5.2. Multi-trigger

Multi-trigger resists appear to be the closest thing to the multi-photon idea applied to DUV or EUV lithigography. A 2018 paper describes the concept as spec "The multi trigger resist (MTR) is a negative tone crosslinking resist that does not need a post exposure bake (PEB)" but gets to multi event property "e reaction will only proceed where an MTR molecule and a crosslinker are simultaneously activated in close proximity to each other" [37] although this work does not appear to show any rate equations or characteristic curves.

Thinking outloud
make sure to come back after doing CAR as the acid dynamics are unclear among other possible problems with the words.

A later paper [36] described some resist design considerations, " resolution, line edge roughness and sensitivity requirements, with minimal defectivity. However, these parameters are linked by a fundamental trade-off in lithography (the RLS triangle) and it is difficult to overcome. For instance, addition of quenchers in chemically amplified resists (CAR) reduces the acid diffusion length and increases the resolution of the patterned features, but decreases the sensitivity, and impacts on material stochastics affecting the line edge roughness. Defectivity due to line collapse, bridging or line breaks is also a fundamental problem."

The authors go on to illustrate the concept with pictures although no obvious reactions or rate equations. From the pictures, the reaction sequence may be,

$X + h\nu \longrightarrow P$
$A \xrightarrow{P} A'$
$B \xrightarrow{P} B'$
$A' + B' \longrightarrow C$
With C being the developer selectivity component. Rate equations would then be,

$$\frac{dX}{dt} = -\phi X \tag{118}$$

$$\frac{dP}{dt} = -\frac{dX}{dt} \tag{119}$$

$$\frac{dA}{dt} = -AP; \frac{dA'}{dt} = AP - \frac{dC}{dt} \tag{120}$$

$$\frac{dB}{dt} = -BP; \frac{dB'}{dt} = BP - \frac{dC}{dt} \tag{121}$$

$$\frac{dC}{dt} = A'B' \tag{122}$$

X and P are straightforward,

$$X = X_0 exp(-\phi t) \tag{123}$$

$$P = X_0(1 - exp(-\phi t)) \tag{124}$$

with A and B being identical but more complicated,

$$\frac{dA}{dt} = -AX_0(1 - exp(-\phi t)) \tag{125}$$

$$-ln(A) = X_0(t + \frac{1}{\phi}exp(-\phi t)) + c \tag{126}$$

$$ln(A) = X_0(-t - \frac{1}{\phi}exp(-\phi t)) + c \tag{127}$$

$$A = A_0 exp(-X_0(t - \frac{1}{\phi}(1 - exp(-\phi t)))) \tag{128}$$

as ϕ goes to zero this seems to have the right limit,

$$A \approx A_0 exp(-X_0(t - \frac{1}{\phi}(\phi t))) \tag{129}$$

Under these conditions A and B are identical leading to

$$\frac{dA'}{dt} = AP - (A')^2 \tag{130}$$

$$\frac{dA'}{dt} = A_0X_0 exp(-X_0(t - \frac{1}{\phi}(1 - exp(-\phi t))))(1 - exp(-\phi t)) - (A')^2 \tag{131}$$

III.6. Multi-trigger with quencher

Perhaps a little more accurately, consider the system with X and Z dead or inactive components,
$A + h\nu \longrightarrow A^*$
$Q + h\nu \longrightarrow X$
$A^* \longrightarrow A$
$A^* + Q \longrightarrow Z$
with the final polymerization step being left vague as issues with strnaded monomers and crosslinking are ignored right now,
$M^+P \xrightarrow{A^*} P$
$M^+M \xrightarrow{A^*} P$
Taking the last process first, assume that a monomer can be attached to anything anywhere and that P regardless of shape or length is left after development,

$$\frac{dP}{dt} = A^*M \tag{132}$$

$$\frac{dM}{dt} = -A^*M \tag{133}$$

The others are straightforward,

$$\frac{dA}{dt} = -A\phi \tag{134}$$

$$\frac{dQ}{dt} = -Qk_q\phi \tag{135}$$

$$\frac{dA^*}{dt} = A\phi - \frac{1}{\tau}A^* - QA^* \tag{136}$$

initial amounts of A,Q, and M are present and maybe drop time constant. As with other cases,

$$A(t) = A_0 exp(-\phi t) \tag{137}$$

$$Q(t) = Q_0 exp(-k_q\phi t) \tag{138}$$

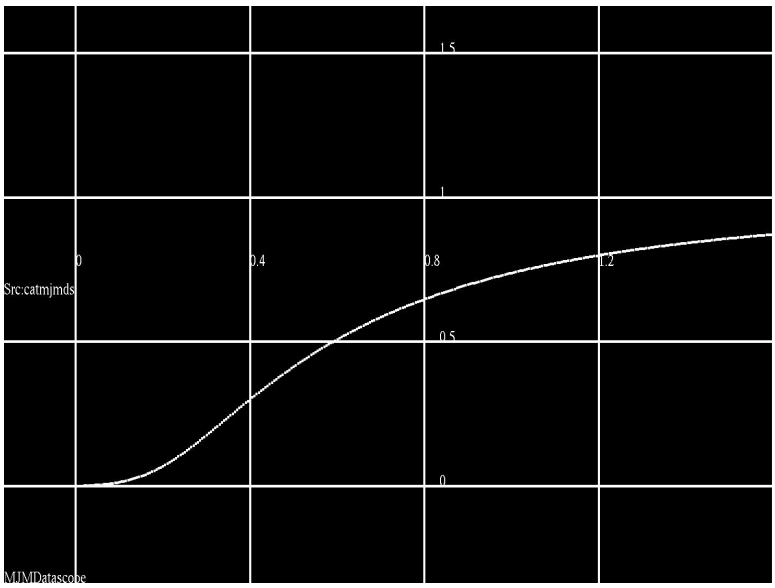


FIG. 11. The quencher is paramterized to be destroyed before the catalyst is activated and destriryed. The initial slope should be zero but if the catalyst is depleted the final amount of polymer is limited below 1. $./mjm\_poisson.out"testtest = mtrigq; a0 = 5; tau = 10; phif = 10; q0 = 100; t = 1; kq = 20; dt = .001"quit$

$$\frac{dA^*}{dt} = \phi A_0 exp(-\phi t) - Q_0 exp(-\phi t)A^* - \frac{1}{\tau}A^* \tag{139}$$

Using an integrating factor,

$$F = (\int (Q_0 exp(-\phi t) + \frac{1}{\tau})dt) \tag{140}$$

$$F = (-\frac{Q_0 exp(-\phi t)}{\phi} + \frac{t}{\tau}) \tag{141}$$

$$A^* = exp(-F)\int (exp(F)A_0 exp(-\phi t)dt) + Cexp(-F) \tag{142}$$

The integral may be doable,

$$I = \int (exp(-\frac{Q_0 exp(-\phi t)}{\phi} + \frac{t}{\tau})A_0 exp(-\phi t)dt) \tag{143}$$

$$I_t = \int (exp(-\frac{Q_0 exp(-\phi t)}{\phi} + \frac{t}{\tau})(A_0 exp(-\phi t) + \frac{A_0}{Q_0 \tau})dt) \tag{144}$$

$$\frac{d}{dt}(exp(-\frac{Q_0 exp(-\phi t)}{\phi} + \frac{t}{\tau})) = (Q_0 exp(-\phi t) + \frac{1}{\tau})exp(F) \tag{145}$$

$$I_t = \frac{A_0}{Q_0} exp(F) \tag{146}$$

IV. SILVER HALIDES

Despite their long history of usage in applications ranging from consumer imaging to X-ray and astronomy applications, a lot remains unknown about the details of latent or developed image formation in silver halide films. A 1980 review did suggest the in real films it took about 4 photons to create an image by a process involving atom motion [4, p. 229] . Several other short reviews exist highlighting other aspects such as grain properties and amplification by up to 10^9 [45].

A turn of the century conference paper reviewed the history and basis for 1,2, and 4 photon mechanisms [26] with the stated interest of optimizing a one photon process due to efficiency.

Thinking outloud
The author mentions Tani who did suggest 2 photon proc
imagers are one photon and have good efficncy as well as
consequence of this mechanism although need to check the

The author outlines a system similar to the cascade above with each photon (equivalent to an electron here) adding to a growing neutral silver cluster,

$Ag_n + Ag^+ + e^- \longrightarrow Ag_{n+1}$

n=4 is thought to be stable and developable while smaller clusters can decay or fail to develop. The net equation is then

$4\,Ag^+ + 4\,e^- \longrightarrow Ag_4$

A two photon process is also described where photo generated holes are converted to electrons but this seems to rely on existing Ag_2 clusters that either already exist or were photogenerated earlier,

$2\,Ag_2(H) + 2\,h^+ \longrightarrow 4\,Ag_4 + 2\,e^-$

or

$2\,Ag^+ + Ag_2 + 2\,e^- \longrightarrow Ag_4$

In considering a one photon process, the author tries to distinguish optical and thermal processes, " This one-photon process thus needs light exposure to provide both the electron and the hole and is not triggered by thermal electron or hole events." Although no idea what this means. In any case, a one photon process was considered using "reduction sensitization centers" or similar electron traps. These mechanisms reduce to $h\nu^+ 2\,Ag_2 \longrightarrow Ag_4 r$ with the use of Au, $AuAg_3{}^+ + e^- \longrightarrow AuAg_3 he$ former equation is thought to have a photon threshold around 1.4eV which the author notes is well above thermal voltages suggesting no dark current but this misses important issues. In any case it is many thermal voltages (typically taken as 26meV not the 30 given here) above the silicon band gap and band-to-band generation may be less for similar quantum efficincies.

Thinking outloud
"do the math" somewhere

IV.1. Notable featues Silver Halides

Superionic conducitivity in AgI [5] which apparently is equivalent to the existence of a Hall Mobility [27] . It appears to persist in compounds such as $C_5H_6NAg_5I_6$ [35].

IV.2. Silver Bromide solid

Copper sulfides can form varying large unit cell crystals with correrpsondingly high integer stoichiometry. They apparently are not molecular crystals. Unit cells may contain 24 or 62 distinct copper atoms and some phases contain a sulphur HCP structure with interstial Cu that become fluid above 100C [10].

V. X-RAY DETECTORS

The EUV has been studied some what but a lot more literature exists on X-ray detectors. While soft X-rays may be somewhat similar to EUV, even the harder X-rays will explore relevant part of the materials including core electrons that may ignored in lower energy studies. This may be important as core electrons and relativistic effects have recently been shown to be important contributors to the potential of the lead acid battery and liely effect EUV resist physics and cheisty.

Halide perovskites are one class of X-ray detector with a recent interest in lead-free versions [47].

Initial discussion on JDFTX issue forum suggested looking at GW/BSE. A quick liteerature search found a few existing and active projects although not all open. Introductory material often introduces the Green Function and self energy in the context of X-ray interactions with matter and several open articles exist. A 2022 work introduces Green's function with Fermi Golden rule progressing to multi-pole and multi-electron with Debye-Waller vibrations results is compared with X-ray absorption and XPS experiments [20]. A 2008 much more detailed paper discusses similar concepts and the code FEFF [39].

A 2024 numeric all electron implementation of GW/BSE used reolution of identity and implemented in not ao opwn FHI-aims code [52]. A 2025 paper used analytical approximations including a multipole-Pade expression for the Green's Function [25]. A 2006 paper introduced the OCEAN code with results mostly above 200 eV [13]. Another short introduction with good match to experiement was a 2007 conference paper [38].

Generally relativistic effects are not mentioned although the Dirac Equation does come up in passing. Usually the ground state is found with DFT which of course could use fully relativistic pseudopotetials. They may be ignored even in heavy elements leading to things like difficulty finding potential of lead-acid battery versus tin [1] . As comparing heavier elements will likely be important including relativity consistently may be worthwhile. QED has also been included in pseudopotential design with reduced core states [51]. Fully relativistic BSE and DCB (Dirac Coulomb Breit) are current topics [11].

Its also likely that results from surface-light interactions and 2D materials will be thought provoking or useful. Surface enhanced interactions with candidate elements such as Ag are well known. Literature here is diverse and may include things like surface enhanced Raman or topological insulators.

Simplifications can rely on approximations or a shift from numerical to more analytical techniques. There is some hope that a more complete physical dscription, fully relativistic with retardation, could lead to some easier analysis but that remains to be demonstrated.

While silver halide literature for nm scale patterning is scarce, there is experience with some pieces. For example, submircon silver clutsters were formed in a mixture of silver and PMMA [24].

AgBr captures the "hole" to make Br and Ag both neutrals and the hole can escape as a gas.

One step in the cluster formation may involve atom migration. The relevance to dark "current" or exposure needs to be considered but also any relevance of the primary EUv energy on related processes.

V.1. sulfur

fluidd copper phase in hcp S lol MoS

V.2. Non-local : grad, erode, dilate, etc

V.3. "Move Towards the Light" the EUV Litho Near Death Experience

While diffusion seems to be inescapable part of photoresist mechanism ion or atom aggregatopm does not seem motivated although it is central to the notions of silver halide latent image formation.

VI. EARLY EVENTS AND ULTIMATE FATE

One important aspect of the lithographic process is the early steps in converting the photon into a latent image. Two processes are commonnly considered. The more common involves creation of a single electron which may thermalize much later. Alternatively several electrons could be created almost simultaneously from the same atom. With the interest in metal oxide resists and the topic of this work being largely silver halides, details of absorption in metals such as silver and tin may be useful to describe and compare where known.

Silver is the immediate issue but tin is of importance too. It appears there are a lot of small issues that likely matter to simple macroscopic results. Its worth noting that just recently the potential of the lead acid battery was explained by adding relativistic terms to the pseudopotential for the valence states [1]. The authors contrast lead to tin by the nuclear charge and then attribute several properties to the additional relativistic effects. Core electrons differ between elements placing different contstraints on outer shell behavior.

Due to the participation of possibly lower level shells in relevant transitions, some DFT pseudopotential calculations may be limited. A variety of specialized techniques exist that may provide details on initial EUV-resist interaction. A Lanczos theory applied to inner shell absorption and photoionization was recently published [33]. Variations on the EOM-CCSD method exist such as an STEOM or similarity transformed approach [6]. One problem seems to be dealing well with the continuum free states which is addressed by several methods [34].

Tables of element EUV absorption coefficients have produced and show several metals including Sn, Sb, Ag, Cs, Bi, Pb have comparably high molar absorption rates along with I [16]. Translation into resist performance of course is complicated by chemical environment and actual fate of the absorbed light energy. Paradoxes and surprises have been observed as mentioned elsewhere. As some resists molecules have dimensions approaching the light wavelength especially with a high dielectric constant various "particle in a box" or antenna effects may be considered. Quantum effects and relativity probably dominate.

A study of oxo caged tin and tin butyl clusters below 70 ev demonsrated a negative tone resist with exposed areas losing organics [42]. The later discussion of Sn-butyl clusters is vaguely similar to the issues with silver halide clusters although many specific are different.

While not directly applicable to photoresist design, a lot of work over the last few decades has explored the photocathode properties of some materials containing high absorption elements. A 1996 work looked at stability and quantum efficiencies of materials such as metal halides such as AgCl and CsI into the 1 nm range [18]. While there was a significant angle dependence of emission its not clear how the test geometry influenced this and if it is relevant at all to photoresist under high NA exposures. Resists would generally want to minimize electron emission and instability may indicate latent image formation. Although if the emitted electron does not cause exposure of random resist, the charging of the exposed region could cause a variety of other effects.

A 2025 work discusses some EUV resist issues and results with silver and gold dry-develop resists with n-heterocycle complexes [21]. While one gold resist was ultimately selected for further evaluation, a neglected story may exist in their figure 2c. In these 3 eposure curves 2 appear more or less exponential while the third one, with 2 Ag centers denoted (i-Pr)L-AuCl demonstrated no response below a threshold of about 100mj/cm2 followed by a concave downward (like $e^n, n < 1$) approach to 1. The authors subsequently dismiss this resist as the PF6 provides better sensitivity. It would be interesting to look at the initial part of these curves to see if there is an observable delay period. Simple "sensitivity" issues should not cause a dealy but rather an exponential over a longer dose range.

Thinking outloud
Also they elaborate on electron thermalization with nice pictures but AFAICT this is really an unknown and needs to be investigated. I became aware of how glib some filler material is from the medial literature. Someone probably said it and it is plausible but never verified although the details here could be important.

As early as 2022 good reviews exists on metal containing e-beam resists with possible utility for EUV. For example, Saifullah et al consider self-developing metal oxide and halide resists and discuss less known mechanisms such as Knotek-Feibelman which can create 3 electrons on impact [43]. They go through metal sulfoxide resists characteristic curves exhibiting a threshold charge dose to begin developing a latent image. Silver is mentioned in passing but not as a halide.

It turns out that lead halides and related perovskites containing organics have been investigated for photovoltaic performance that provides some information on EUV issues. One recent work suggests they have a lot of remarkable properties and go on to do some analysis in the EUV region [14]. While the goals of these efforts are to produce stable energy sources, their susceiptibility to decomposition under illumination is exactly a desired feature of a photoresist. Both lead and iodine have decent EUV absorption and the possibilities of designing conversion of light into decomposition may be worth exploring.

Its also worth keeping in mind while exploring resist candidates that the resist itself could form the desired features such as conductors. This process has been explored in a set of techniques called direct optical lithogrphy[50]. As

several resists begin with metal compounds that become more metallic in exposed areas the potential is there to directly form condcutors.

An earlier thesis from 2016 explored an HfO resist which appeared to use sulfate to control aggregation [28]. The resist was also explored for response to electrons and found to response to energies as low as 2eV with a high enough dose although later XPS analysis of sulfur content suggests some details need to be explored. A 30kev He+ ion beam was also found to work with 50-100 times more sensitivity than 30kev electrons. In the reiew of past methods, this thesis also mentions Ag_2S and similar resists and their limitations.

VII. CONCLUSIONS

VIII. SUPPLEMENTAL INFORMATION

VIII.1. Computer Code

```
picture from datascaope,

 2068 ./mjm_poisson.out -cmd "plot 0 10 .1 3 3" -cmd quit
 2069 ./mjm_poisson.out -cmd "plot 0 10 .1 30 3" -cmd quit
 2070 ./mjm_poisson.out -cmd "plot 0 100 .1 30 3" -cmd quit
 2071 ./mjm_poisson.out -cmd "plot 0 10 .1 1 3" -cmd quit
 2072 history
```

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2. Free software including Linux, R, LaTex etc.

3. Some discussion with Frederick Chen on Linked In [7].

4. Some discussion with Alex Robinson [41]

5. Thanks everyone who contributed incidental support.

Appendix A: Statement of Conflicts

No specific funding was used in this effort and there are no relationships with others that could create a conflict of interest. I would like to develop these ideas further and have obvious bias towards making them appear successful. Barbara Cade, the dog owner, has worked in the pet food industry but this does not likely create a conflict. We have no interest in the makers of any of the products named in this work.

Appendix B: About the Authors and Facility

This work was performed at a dog rescue run by Barbara Cade and housed in rural Georgia. The author of this report ,Mike Marchywka, has a background in electrical engineering and has done extensive research using free online literature sources. I hope to find additional people interested in critically examining the results and verify that they can be reproduced effectively to treat other dogs.

Appendix C: Some Math Stuff

Bimolecular recomination for example,

$$\frac{dA}{dt} = A - A^2 \tag{C1}$$

you can guess something like

$$A = \frac{1}{t+f} \tag{C2}$$

and get

$$\frac{df}{dt} = -(t+f) \tag{C3}$$

which can be solved with an integrating factor giving

$$A = \frac{1}{1+Ce^{-t}} \tag{C4}$$

actually better was partial fractions ,

$$\frac{dA}{A(1-A)} = dt \tag{C5}$$

leading to same results doh.

Appendix D: Symbols, Abbreviations and Colloquialisms

TERM definition and meaning

Appendix E: General caveats and disclaimer

This document was created in the hope it will be interesting to someone including me by providing information about some topic that may include personal experience or a literature review or description of a speculative theory or idea. There is no assurance that the content of this work will be useful for any paricular purpose.

All statements in this document were true to the best of my knowledge at the time they were made and every attempt is made to assure they are not misleading or confusing. However, information provided by others and observations that can be manipulated by unknown causes ("gaslighting") may be misleading. Any use of this information should

be preceded by validation including replication where feasible. Errors may enter into the final work at every step from conception and research to final editing.

Documents labelled "NOTES" or "not public" contain substantial informal or speculative content that may be terse and poorly edited or even sarcastic or profane. Documents labelled as "public" have generally been edited to be more coherent but probably have not been reviewed or proof read.

Generally non-public documents are labelled as such to avoid confusion and embarassment and should be read with that understanding.

Appendix F: Citing this as a tech report or white paper

Note: This is mostly manually entered and not assured to be error free.
This is tech report MJM-2025-002.

Version	Date	Comments
0.01	2025-05-01	Create from empty.tex template
-	October 4, 2025	version 0.00 MJM-2025-002
1.0	20xx-xx-xx	First revision for distribution

Released versions,
build script needs to include empty releases.tex

Version	Date	URL

@techreport{marchywka-MJM-2025-002,
filename ={euvnoise} ,
run-date ={October 4, 2025} ,
title ={EUV Lithography : Don't take my kodachrome away} ,
author ={Mike J Marchywka } ,
type ={techreport} ,
name ={marchywka-MJM-2025-002} ,
number ={MJM-2025-002} ,
version ={0.00} ,
institution ={not institutionalized, independent } ,
address ={ 157 Zachary Dr Talking Rock GA 30175 USA} ,
date ={October 4, 2025} ,
startdate ={2025-05-01} ,
day ={4} ,
month ={10} ,
year ={2025} ,
author1email ={marchywka@hotmail.com} ,
contact ={marchywka@hotmail.com} ,
author1id ={orcid.org/0000-0001-9237-455X} ,
pages ={ 31}
}

Supporting files. Note that some dates,sizes, and md5's will change as this is rebuilt.

This really needs to include the data analysis code but right now it is auto generated picking up things from prior build in many cases

```
2737 Sep 21 07:29 comment.cut 2b7b3d43b2832ccf5ea2a8778155f9af
1660461 Jul 31 04:27 ../copper/copper.bib 985b4db2ba9a919beb68089accca4b1b
17655 Sep 21 07:29 euvnoise.aux 525b1d4b9e1e06de5bba32cee6fc3a0a
19104 Sep 21 07:29 euvnoise.bbl 798819b2dec759908105b8c497113c1c
181949 Sep 21 07:29 euvnoise.bib d6ba7711db33ac0a123d19310fd60154
3210 Sep 21 07:29 euvnoise.blg 26ffb44c856501bc4c30a1b2580875a2
0 Sep 21 07:33 euvnoise.bundle_checksums d41d8cd98f00b204e9800998ecf8427e
```

```
27121 Sep 21 07:29 euvnoise.fls cae211d4c7a467ab15df6ed686466c84
3 Sep 21 07:29 euvnoise.last_page 22cab69bca05d296a2d779a52cdee643
56963 Sep 21 07:29 euvnoise.log 1f231ee30c9ac659629e84c8838a41e9
0 Sep 21 07:29 euvnoiseNotes.bib d41d8cd98f00b204e9800998ecf8427e
6836 Sep 21 07:29 euvnoise.out 3c5fc233f17b342f240115b50e2725a3
446862 Sep 21 07:29 euvnoise.pdf ac6e8b1188741fcfce9b6f6c05a75a73
21901 Sep 21 07:29 euvnoise.tex 7691afd1d1223e34873893511ef540ad
3087 Sep 21 07:29 euvnoise.toc c36eb48ff0e35391d65d2f9cdd77c516
48207 Jun 23 14:50 /home/documents/latex/bib/mjm_tr.bib c1e418073aff2480bc78f63905450638
48988 Jul 1 14:18 /home/documents/latex/bib/releases.bib f2fdf87a36feddccbab0918dc2b00129
7331 Jan 24 2019 /home/documents/latex/pkg/fltpage.sty 73b3a2493ca297ef0d59d6c1b921684b
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