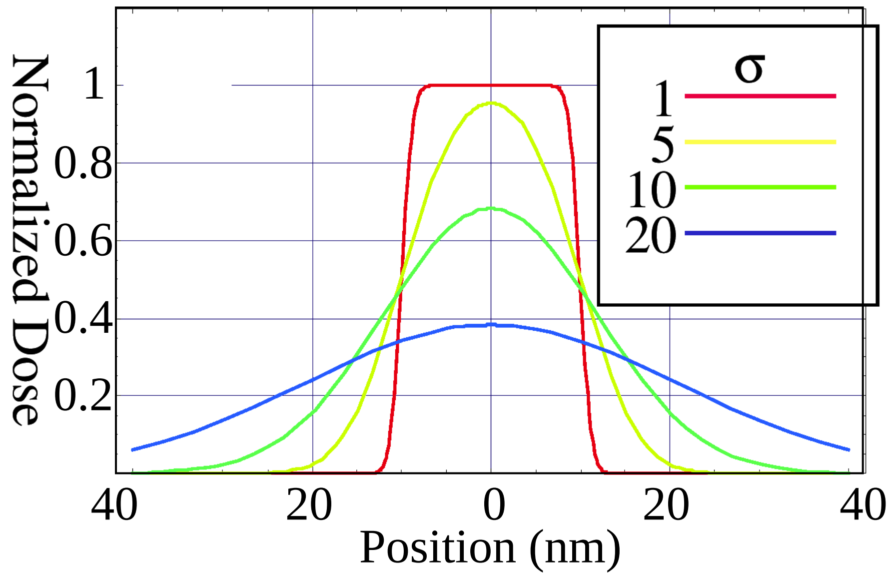
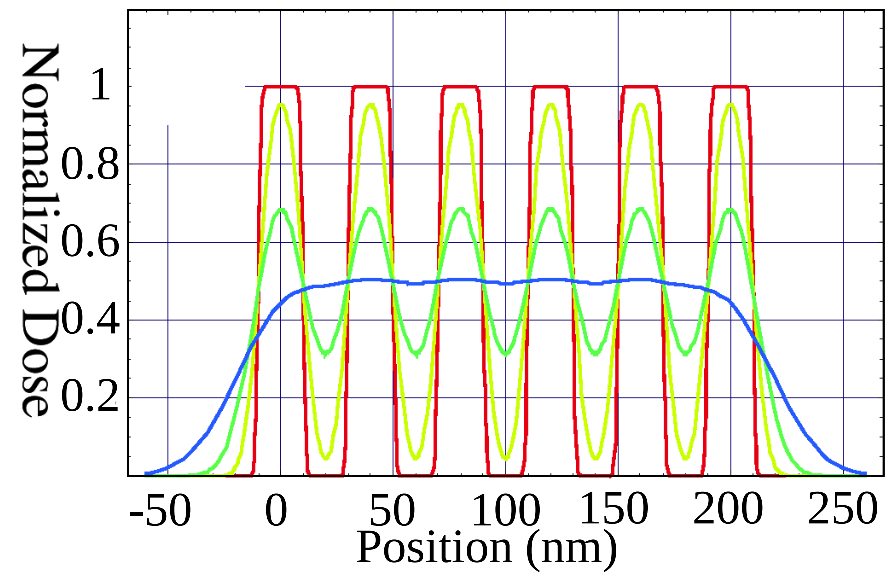
Resist Materials II

- Resolution
  - Aerial Image
    - Dose latitude
  - Statistical considerations
    - Sensitivity Limits
  - Energy Deposition Distribution
    - Beam broadening
    - Energy and chemistry
  - Development
    - Diffusion in CA materials
    - Line edge roughness
  - Limits to resolution

Resolution – Aerial Image



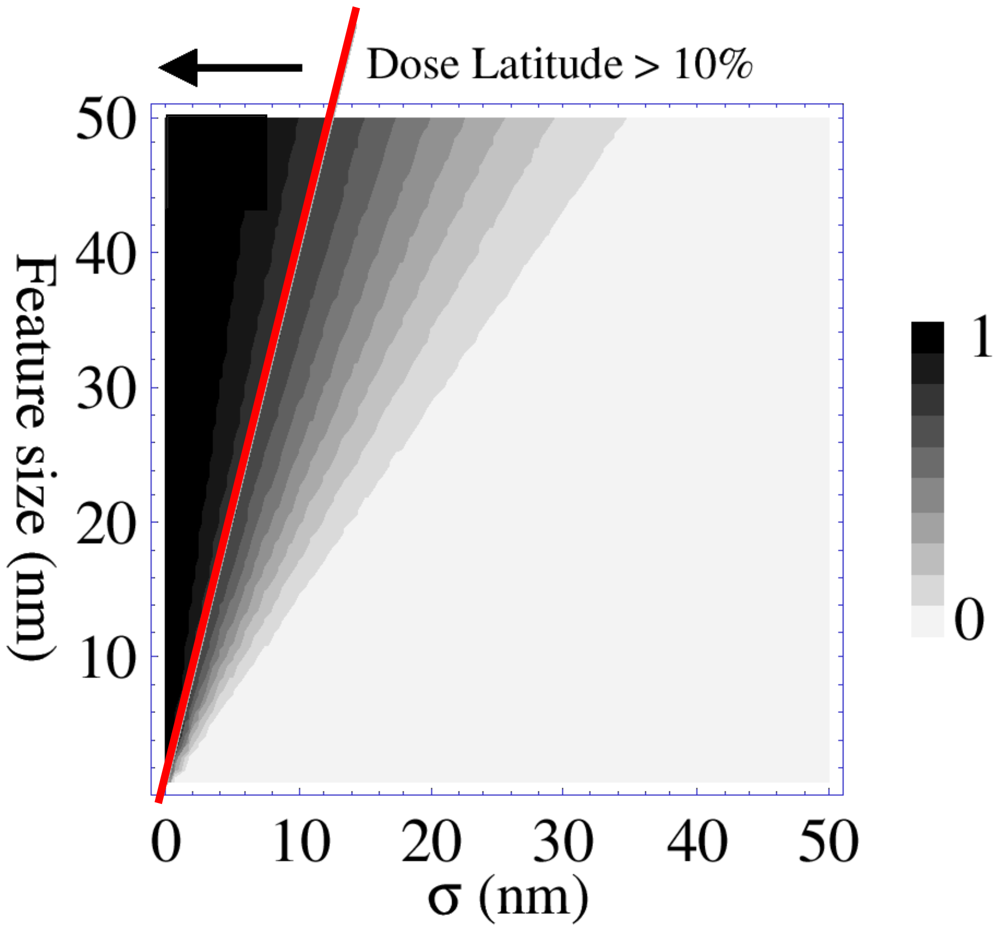
20 nm isolated feature



20 nm lines & spaces

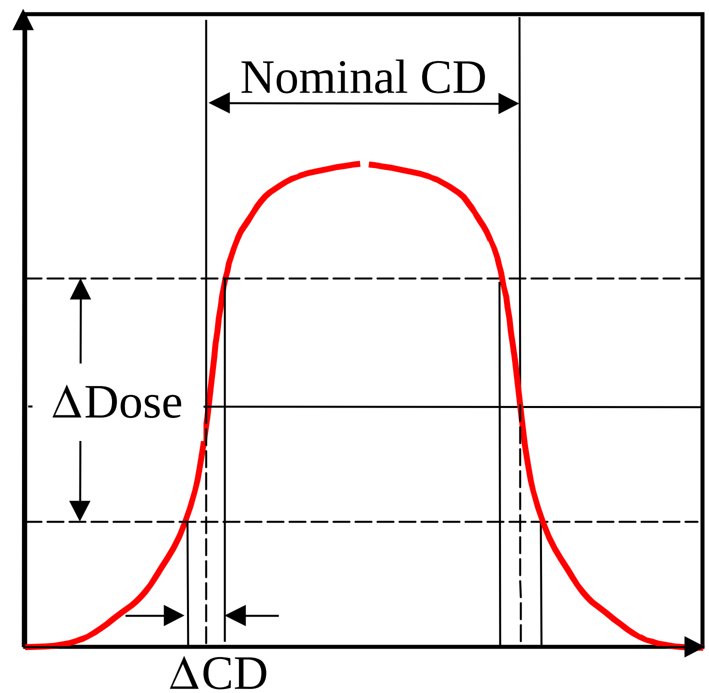
- The aerial image represents the ideal intensity distribution that can be formed by a lithography system
  - Measured immediately above the wafer, before any interaction with resist or substrate
- Aerial image resolution controls printable feature size
  - Modulation falls to ≈ zero when $\sigma > \sqrt{2Ln2}$ feature size

Dose Latitude



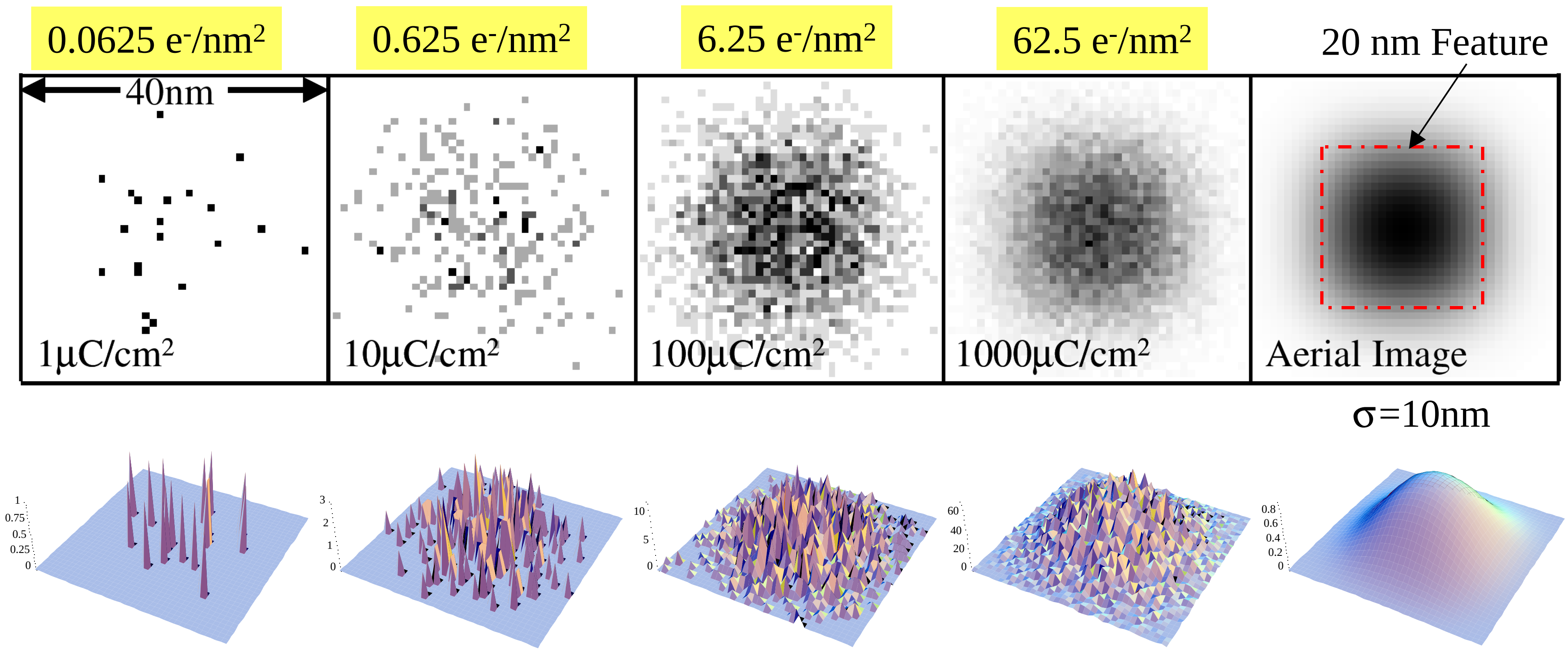
Normalized Modulation Transfer Function

- Robust process requires dose latitude (ΔDose ±10%ΔCD) > 10%
  - Blur (σ) < 20% CD



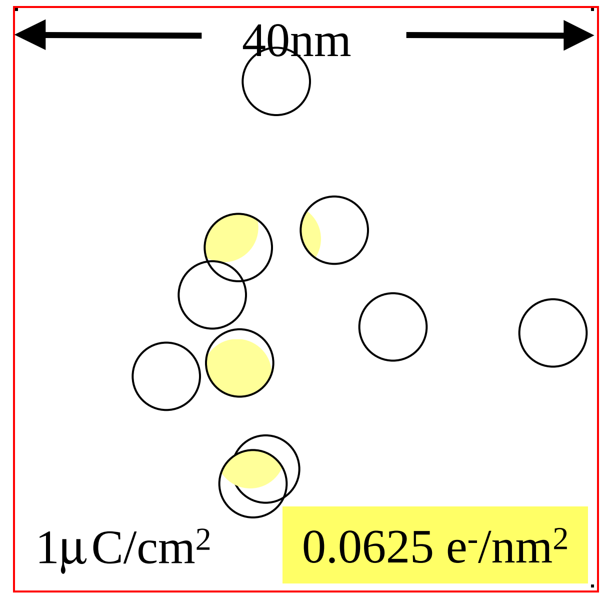
Resolution - Statistics I

- High sensitivity ➢ small numbers of electrons
- Exposure statistics can lead to large variations in feature size



Resolution - Statistics II

- Simple calculation: each electron exposes cylinder of material
  - Resolution = mean separation between electrons, δ
  - 1 μC/cm^2 ➢ δ = 4 nm
- Electrons in a bucket: probability feature fails to print < 10^{-15}
  - Feature fails to print if dose is < 0.5 dose to print on size
  - Probability is < 10^{-15} when number of electrons > 200
  - Dose = 8 μC/cm^2 for 20 nm features
- Signal to noise: $\sqrt{N}/N < X\%$ - what is X?



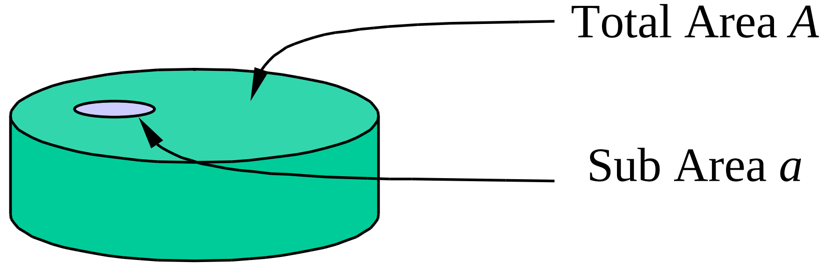
Shot-noise - Poisson Statistics

<u>Example</u>

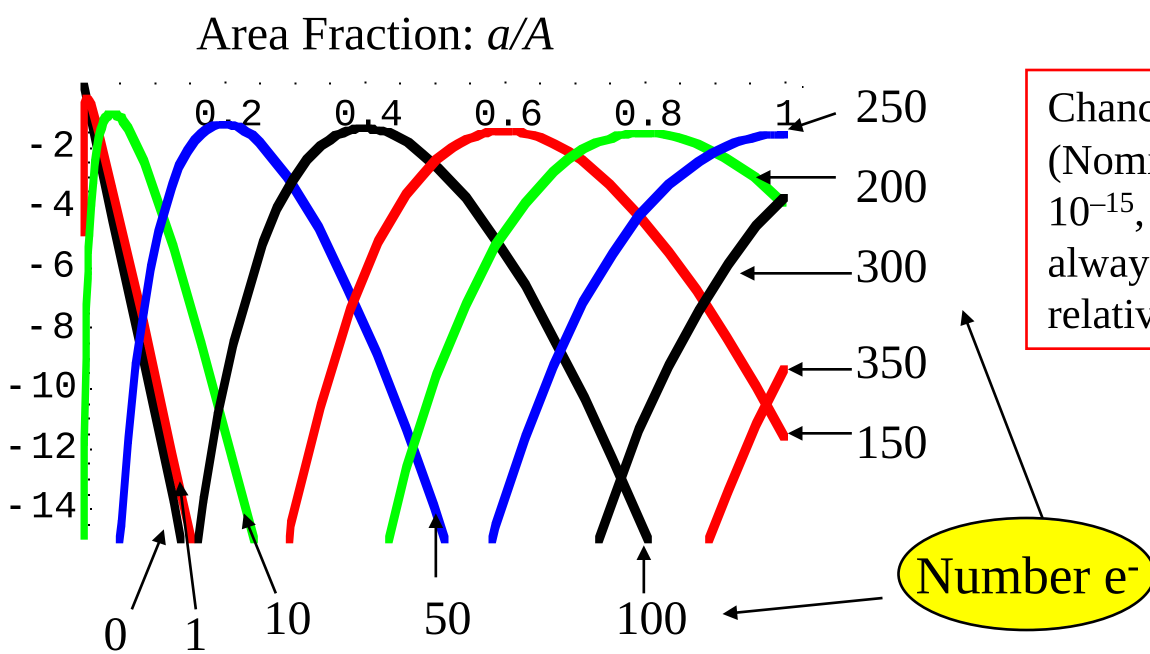
Let Intensity = defocus tophat in projection electron system
35nm diameter and 4 $\mu C/cm^2$

$\Rightarrow$ IAt = 250 electrons

(Nominal dose to print on size = 2 x dose to clear)



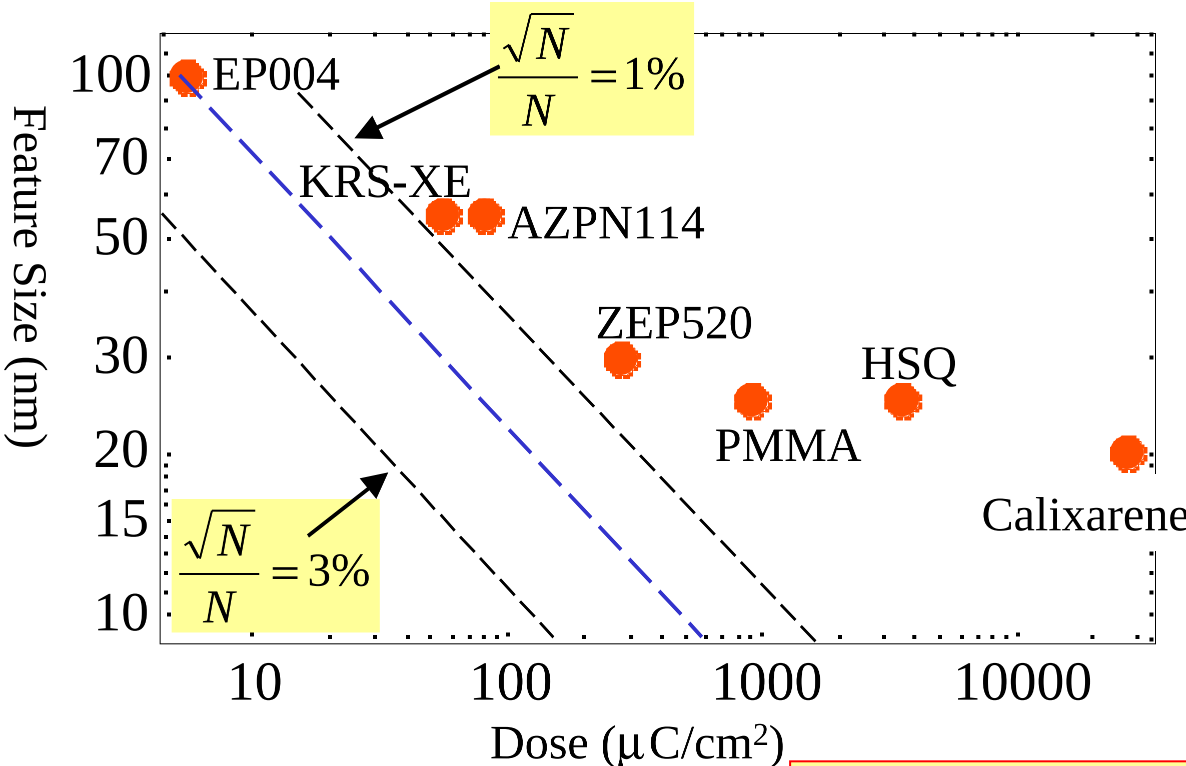
Log of the Probability to get n particles in the given area fraction



Chance of getting ≤ half (Nominal Dose) is << 10^{-15}, i.e. features will always print & dose is relatively uniform

Observed Resolution vs Dose

$$N = \frac{Dose \cdot L^2}{e} \Rightarrow L = \sqrt{\frac{eN}{Dose}}$$

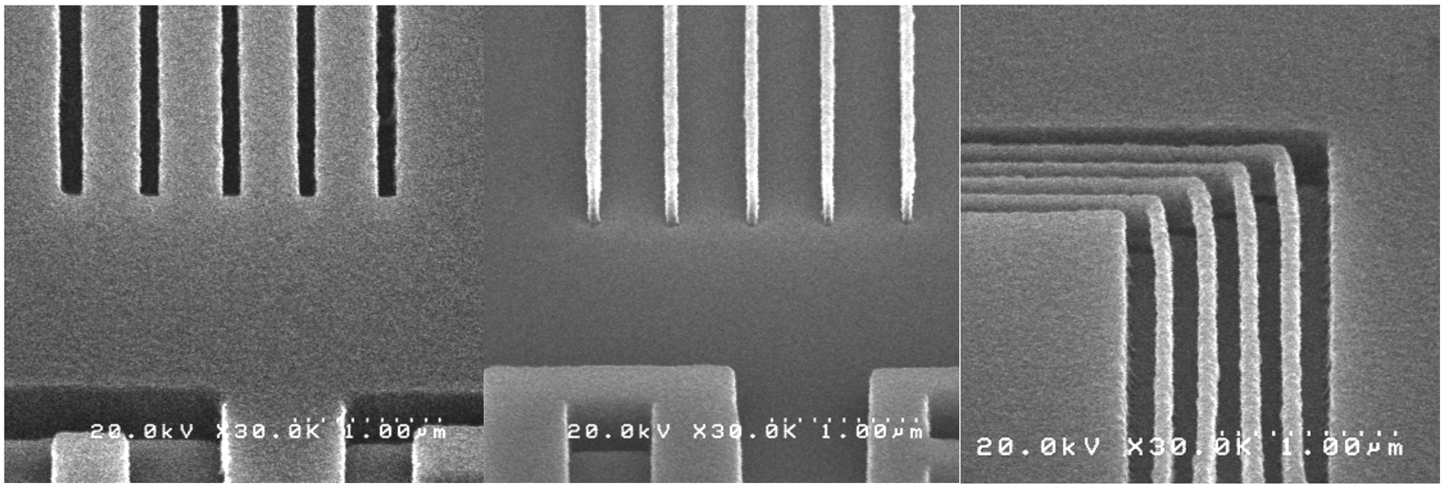


- Key assumptions:
  - Arrival statistics
    - ➢ chemistry
  - No other sources of blur
- CA materials PAG = 5%
  - PAG "scavenges" electrons
- Blur from aerial image, electron resist/substrate interactions, chemistry

$$\sigma_{total} = \sqrt{\sigma_{image}^2 + \sigma_{chemistry}^2 + \sigma_{scattering}^2 + \sigma_{statistics}^2}$$

Advanced Resist Results

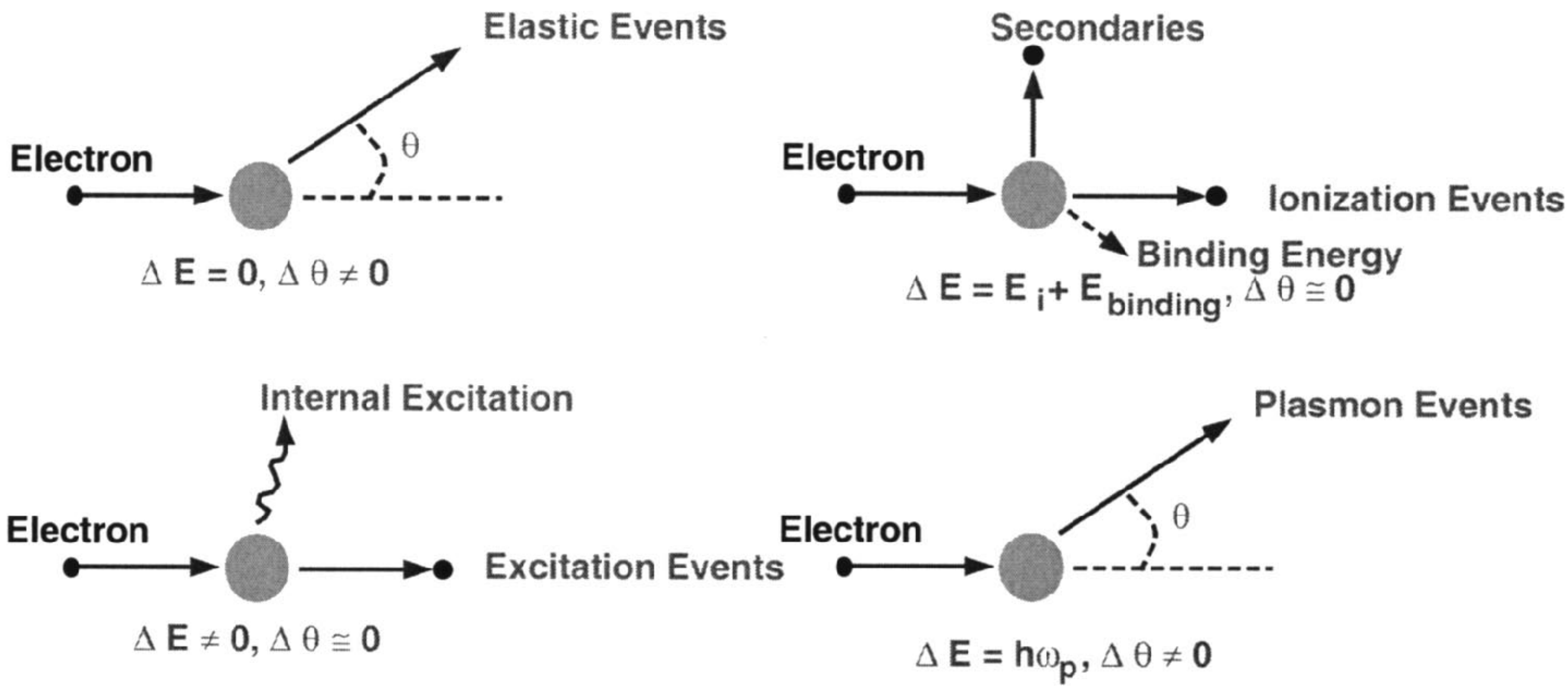
100 kV SCALPEL exposures



80 nm, 5.8 $\mu C/cm^2$ | 80 nm, 5.8 $\mu C/cm^2$ | 100 nm, 5.4 $\mu C/cm^2$

5.4 $\mu C/cm^2$ @ 100 nm feature size = 3375 electrons/100 nm pixel, $\sqrt{N}/N$ = 1.72%

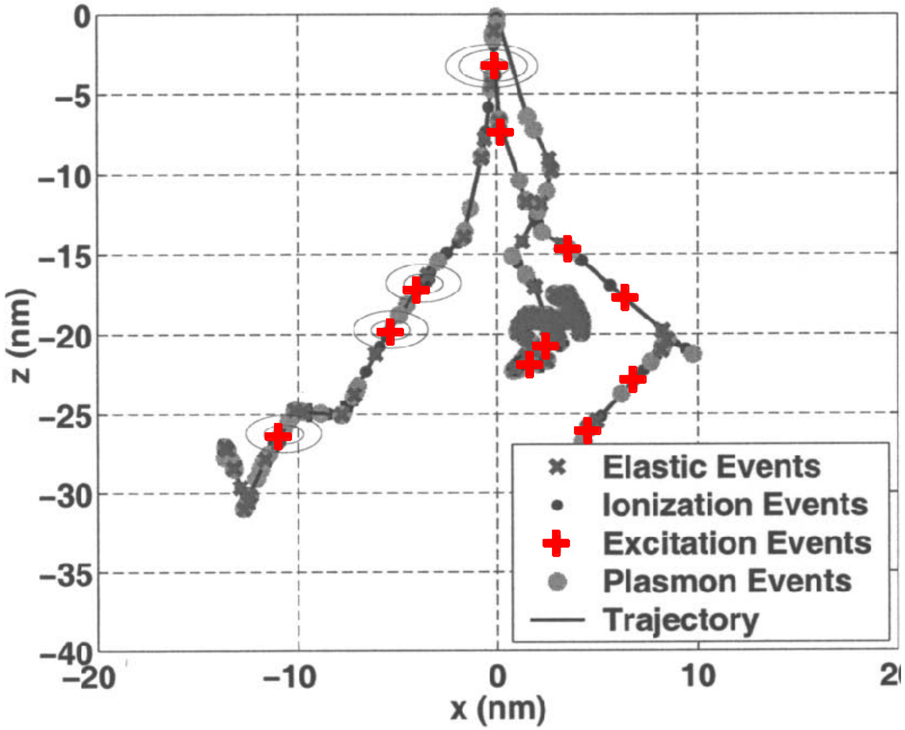
Energy Deposition I



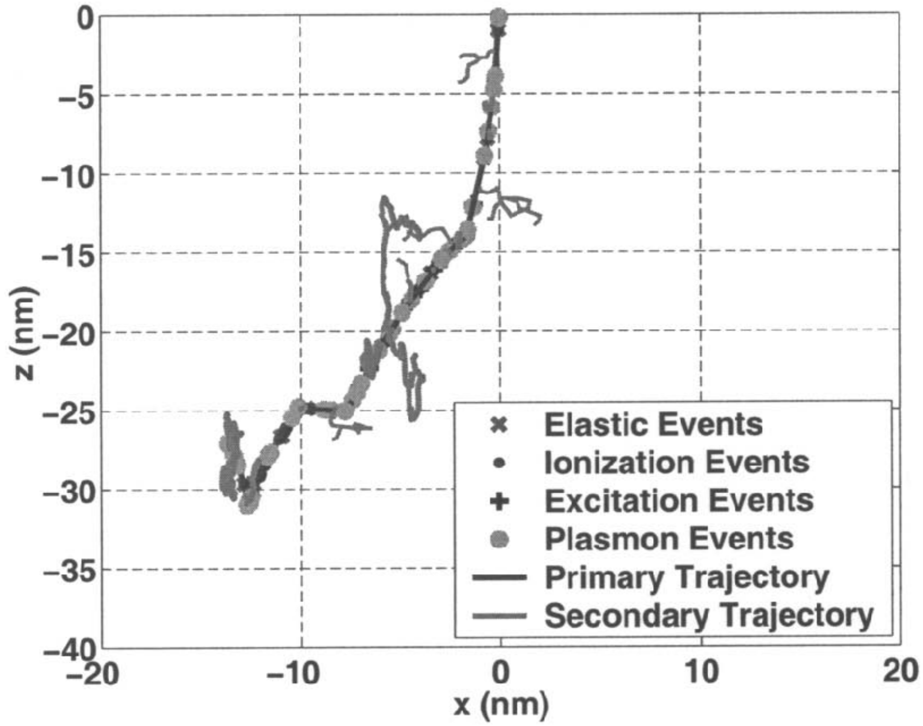
- Of the four different kinds of scattering events only two - excitation & ionization - result in chemical changes

"Comprehensive model of electron energy deposition", G. Han, M. Khan, Y. Fang, and F. Cerrina, *J. Vac. Sci. Technol.*, **B20** p2666 (2002)

Energy Deposition II



Trajectories of 3 primary 1keV electrons



Trajectories of 1 primary 1keV electrons and associated secondary electrons

- Excitation events are low energy and thus have large cross-sections, i.e. are substantially delocalized
- Secondary electrons also result in a substantial broadening of deposited energy profile

"Comprehensive model of electron energy deposition", G. Han, M. Khan, Y. Fang, and F. Cerrina, *J. Vac. Sci. Technol.*, **B20** p2666 (2002)

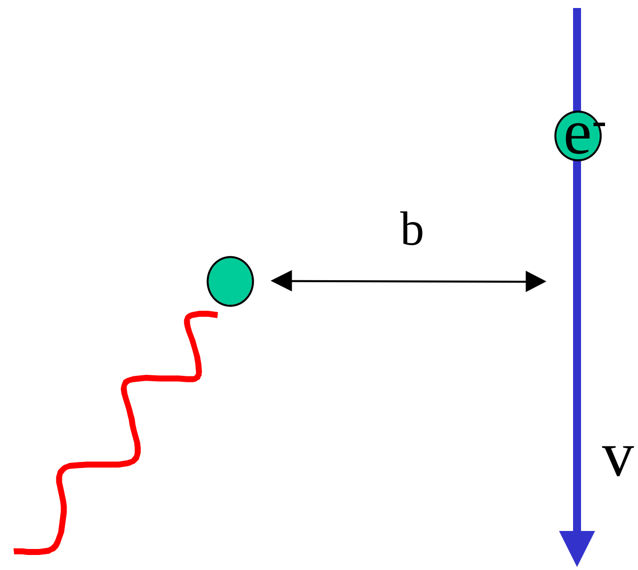
Energy Deposition III

- Pulse received by stationary electron has duration b/v
- Pulse contains Fourier components up to $\omega = v/b$
- Able to generate energy losses, $\Delta E \leq hv/2\pi b$
  - $b \leq hv/(2\pi\Delta E)$
- At 100 keV, $v = 1.6\text{x}10^{8}\ \text{ms}^{-1}$

$\Delta E = 5$ eV, b = 10 nm

$\Delta E = 50$ eV, b = 1 nm

$\Delta E = 500$ eV, b = 0.1 nm



$b \leq hv/(2\pi\Delta E)$

Energy Deposition vs Acid Generation in CA Materials

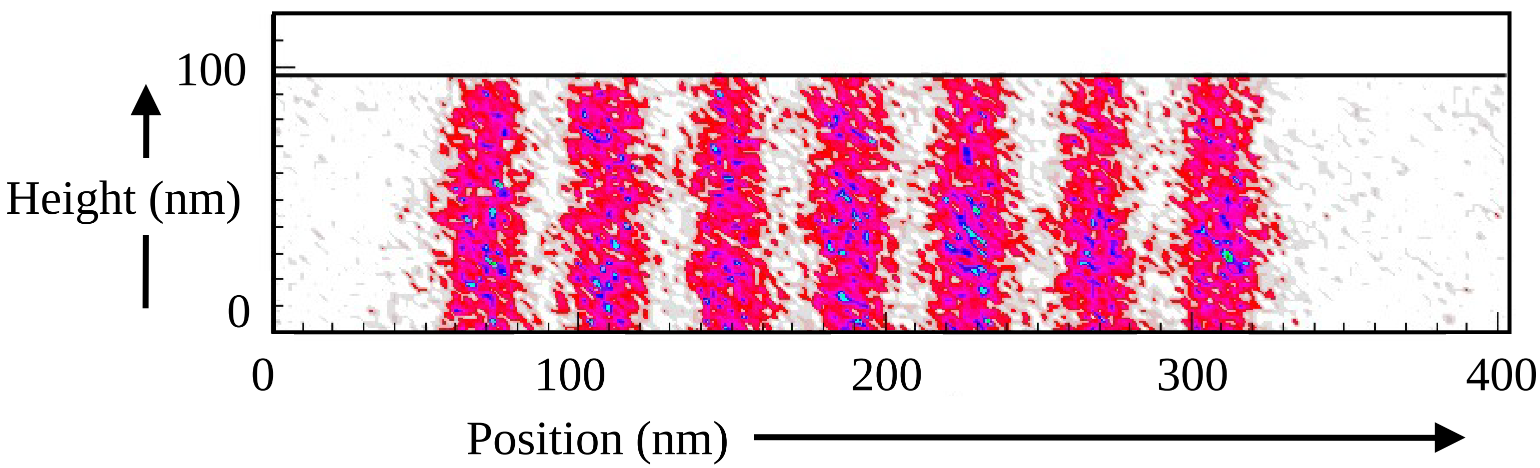
- Energy absorption process produces an ionized molecule, typically from the base resin
  - $RH \xrightarrow{h\nu} RH^{+}_{\bullet} + e^{-}, \quad RH^{+}_{\bullet} + e^{-} \longrightarrow RH^{*}$
  - In a non-polar material, electrons recombine with counter-cation
- Electrons that escape recombination eventually thermalize
- Polar acid generator molecules effectively "scavenge" electrons
  - ➢ Ionization probability for acid generator is, to some extent, decoupled from fraction of PAG molecules
  - ➢ Acid formation occurs some distance (several nm) from site of energy absorption

"Study on Radiation-Induced Reaction in Microscopic Region for Basic Understanding of Electron Beam Patterning in Lithographic Process I - Development of Subpicosecond Pulse Radiolysis and Relation Between Space Resolution and Radiation Induced Reaction of Onium Salt", T. Kozawa, A. Saeki, Y. Yoshida and S. Tagawa, *Jap. J. Appl. Phys.*, **41** p4208 (2002)

"Study on Radiation-Induced Reaction in Microscopic Region for Basic Understanding of Electron Beam Patterning in Lithographic Process II - Relation Between Resist Space Resolution and Space Distribution of Ionic Species", A. Saeki, T. Kozawa, Y. Yoshida and S. Tagawa, *Jap. J. Appl. Phys.*, **41** p4213 (2002)

Energy Deposition Distribution

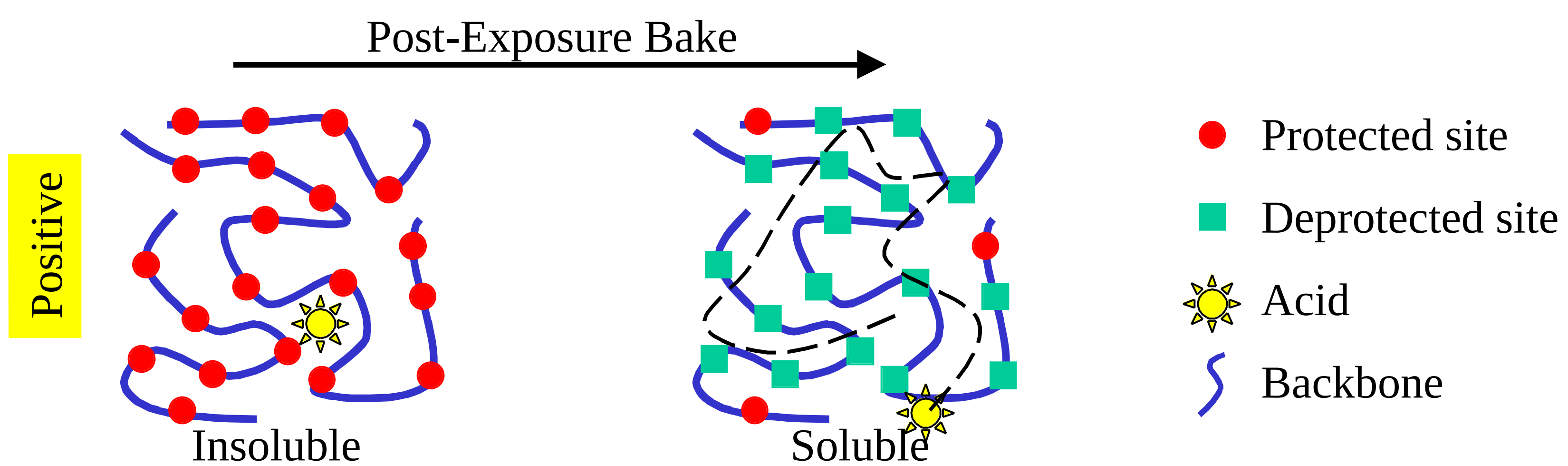
- At high voltages (100 kV) and in thin (100 nm) resists, forward scattering is 5 – 10 nm (90% energy contour diameter) at the base of the film
- Exposure is accomplished by secondary electrons which peak in number at 10 eV
  - Mean free paths of a few nanometers
- ➢ Even with very finely focused beams resolution is limited by the nature of the electron solid interactions



Monte-Carlo simulation of the energy deposition distribution for 20 nm lines & spaces. δ-function incident beam assumed. 20 $\mu C/cm^2$ dose.

Chemically Amplified Resists - Diffusion I

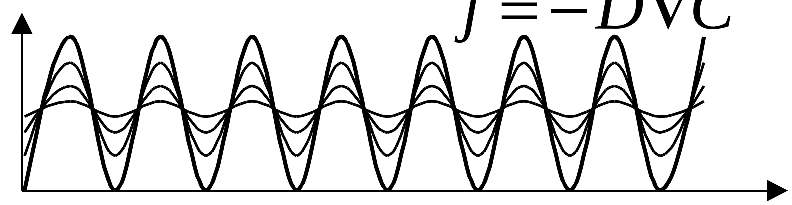
- Acid diffusion in CA materials is highly complex:
  - Motion of H^+ affected by anion and by polar functionalities of resist
    - Diffusion coefficient changes with extent of deprotection reaction
    - Catalytic chain lengths can be > 1000
    - However, diffusion distances can be as small as 5 nm



Chemically Amplified Resists - Diffusion II

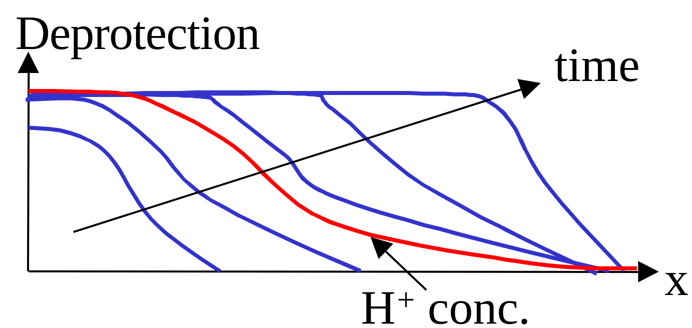
- Acid concentration profile formed upon exposure - diffusion will homogenize distribution
- Reaction-diffusion model accounts for changing diffusion coefficients as deprotection reaction proceeds and material changes from non-polar to polar, for changing deprotection rates as concentration of protecting groups changes and for reduction of acid concentration through various loss mechanisms
  - Diffusion coefficients for TBI-PFBS at 105 °C in PTBOCST: **15 nm^2/s** (protected), **0.1 nm^2/s** (deprotected). Smaller PAG anions allow faster diffusion.
  - Deprotection reaction proceeds (slowly) even at low acid concentrations ⇒ blurring
  - Base added to films to reduce acid levels in nominally unexposed areas

$$j = -D\nabla C$$



$$\frac{\partial C}{\partial t} = -\nabla(D\nabla C)$$

Concentration dependent diffusion



“Chemical and Physical Aspects of the Post-Exposure Baking Process Used for Positive-Tone Chemically Amplified Resists”, W.D. Hinsberg, F.A. Houle, M.I. Sanchez and G.M. Wallraff, *IBM J. Res. & Dev.*, **45** p667 (2001)

“Method of Measuring the Spatial Resolution of a Photoresist”, J.A. Hoffnagle, W.D. Hinsberg, M.I. Sanchez and F.A. Houle, *Optics Letters*, **27** p1778 (2002)

Statistics of Resist Roughness

Process Flow ⇒ Multiple Statistics

- Dose Statistics: Probability distribution for # of electrons/"pixel".
- Acid Release Statistics: Probability of Acid Release given presence of an electron.
- PEB Statistics: Probability of deprotection given Acid Random Walk
- Dissolution Rate Statistics: Concatenate above statistics
  Deprotection/Acid Density,
  Dissolution Rate/Deprotection Density…
- Surface Statistics: Compute Surface Evolution using Rate Statistics

Assume Positive Chemically Amplified Resist
Straightforward modification for negative resist

"Analytical Model of the 'Shot Noise' Effect in Photoresist", G.M. Gallatin and J.A. Liddle, *Microelectronic Engineering*, **46** p365 (1999)
"Continuum Model of Shot Noise and Line Edge Roughness", G.M. Gallatin, *Proc. SPIE*, **4404** p123 (2001)

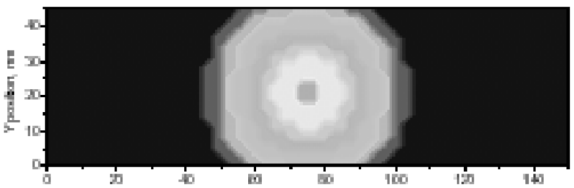
Line Edge Roughness

- Roughness depends directly on dissolution rate
  - Exposure ⊗ Latent Image ⊗ PEB statistics washes out effect of shot-noise
- LER increases with decreasing image edge slope
- Minimum value of roughness is related directly to granularity of resist
  - In conventional materials, the size of a molecule
  - In CA materials, the molecular size or the volume deprotected by an acid molecule during PEB (links resolution and sensitivity)

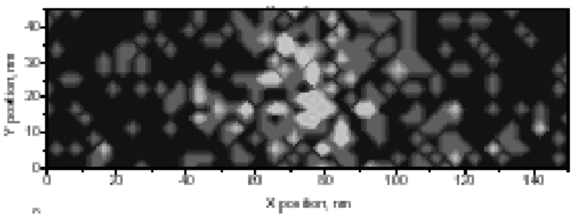
LER Simulation

48 nm contact

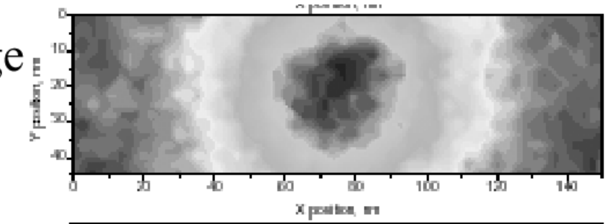
Intial acid image



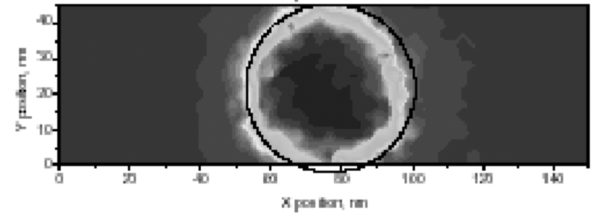
Acid after PEB



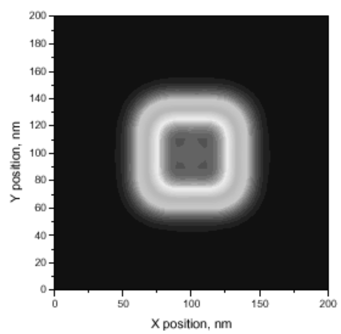
Resist image after PEB



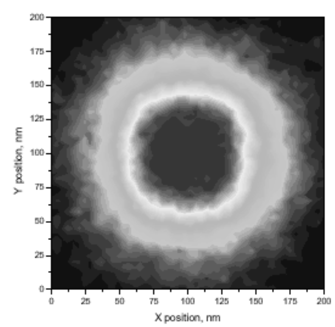
Developed contact



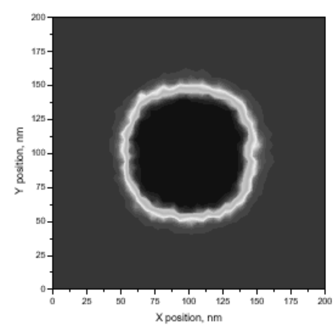
Photons



Deprotected Polymer



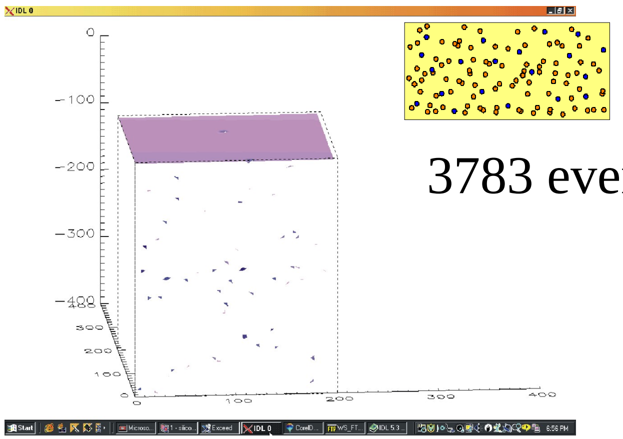
Dissolved Polymer



- Influence of different stages of image formation process in a chemically amplified resist on the final, developed feature

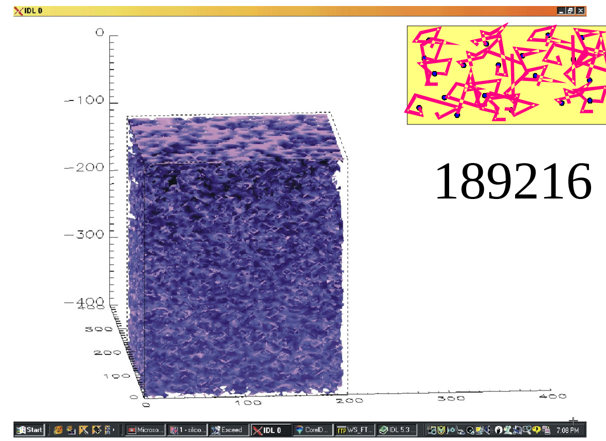
"The Estimated Impact of Shot Noise in Extreme Ultraviolet Lithography", J. Cobb, F. Houle and G. Gallatin, to appear in *Proc. SPIE*, Microlithography Conference (2003)

Step-by-step Image Formation in EP-004 at 3 μC/cm²



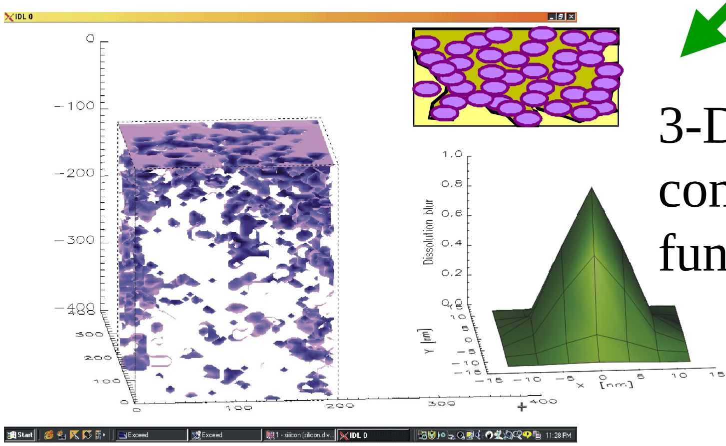
3783 events

- Photoacid events



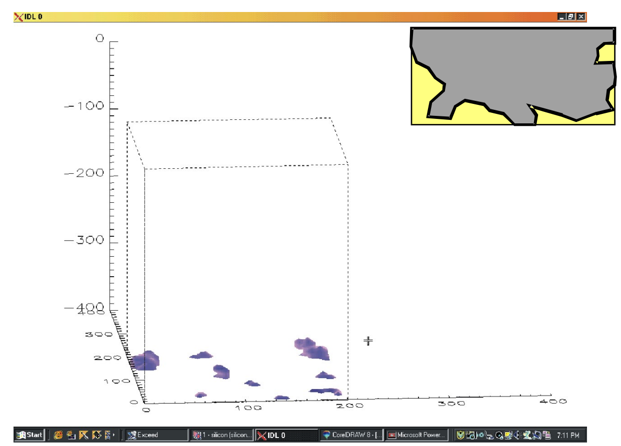
189216 events

- Amplification events



3-D convolution function

- Solubility change

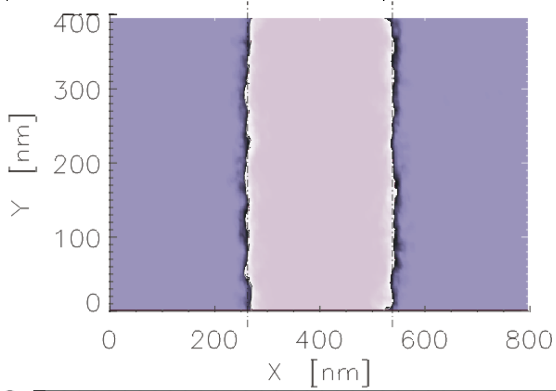


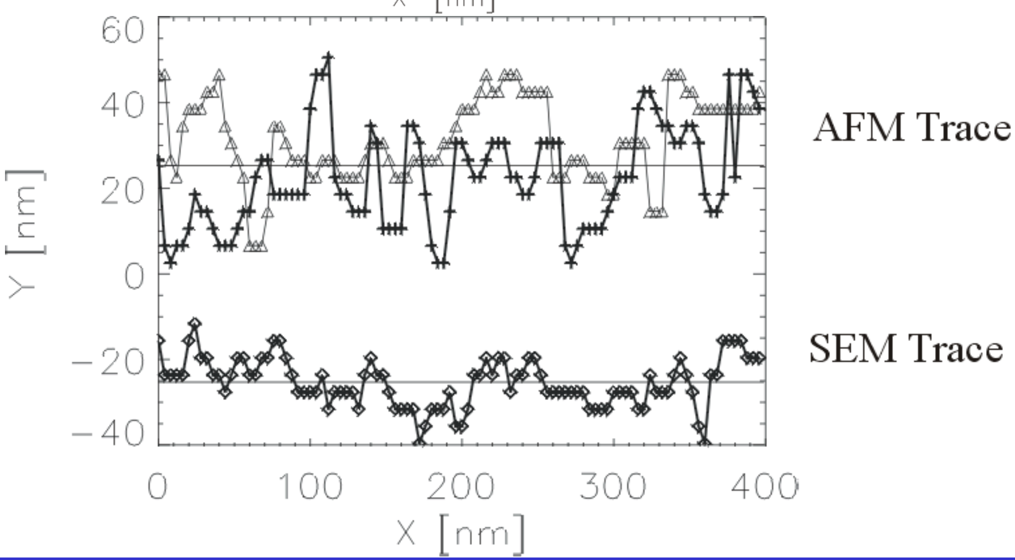
- Development

"Reist Requirements for Electron Projection and Direct Write Nanolithography", L.E. Ocola, Mat. Res. Soc. Symp. Proc., **705** Y1.1.2 (2002)

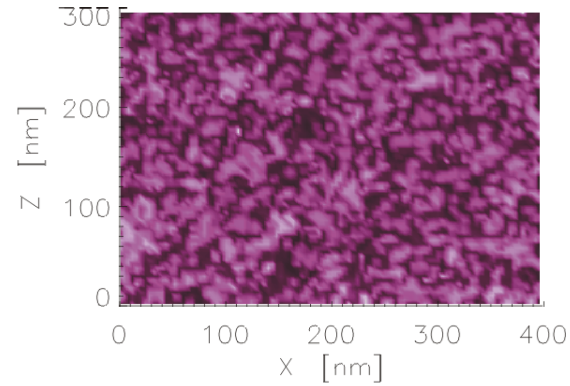
Simulated SEM & AFM LER of a Resist Feature

- Simulated SEM image (50% threshold)





- Simulated AFM sidewall image



- AFM LER (1σ):
  - Simulated: 10.7 nm
  - Experiment: NA
- SEM LER (1σ):
  - Simulated: 5.7 nm
  - *Experiment: 3 nm*

L.E. Ocola

Performance Limits

- Resolution and sensitivity are strongly coupled
- Resolution is determined by

$$\sigma_{total} = \sqrt{\sigma^2_{image} + \sigma^2_{chemistry} + \sigma^2_{scattering} + \sigma^2_{statistics}}$$

- Image blur can be reduced to 0.5 nm
- Statistical blur can be reduced by going to high doses
- Chemical blur can be reduced by using non-CA materials or curtailing acid diffusion
- Scattering blur can only be reduced by changing the nature of the electron solid interactions
  - High energy processes are localized to the incident beam
    - Hole drilling in inorganic resists
    - Radiation damage in $Si0_2$

"Resist Requirements and Limitations for Nanoscale Electron Beam Patterning", J.A. Liddle, G.M. Gallatin and L.E. Ocola, Mat. Res. Soc. Symp. Proc. (2002)
"Resolution Limits for Electron-Beam Lithography", A.N. Broers, *IBM J. Res. Develop.*, **32** p502 (1988)