NACK NETWORK

For Nanotechnology Workforce Education

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Patterning for Nanotechnology

E SC 214

Unit 1
Advanced Lithography
General Information

Lecture 1
Some Basics of Photolithography

Outline

- General Resist Information
- Negative Resists
- Positive Resists
- Primer Technologies
- Resist Application
- Electromagnetic Spectra
- Post-exposure Bake
- Development

Photoresist

- Resist is the “energy sensitive” chemical spun-on to the substrate’s surface that serves two purposes
  - Act as a medium to absorb a pattern upon exposure
  - Provide protection for unpatterned portions of the substrate
- Since the resists used in contact lithography are light sensitive, they are called *optical* resists or **photoresists**
- Photoresist must have good adhesion to the substrate’s surface

Photoresist

- Modern nanofabrication devices require a high **resolution capability**
  - The smallest feature that can be produced in a resist layer
  - The smaller the feature capability of the resist, the higher the resolution capability
  - Smaller features require a thinner resist layer, but this layer must still be thick enough to act as a barrier for further processing

Resists

- Photoresist
  - Positive- popular
  - Negative- historically viewed as a health risk
- Positive
  - UV radiation cuts polymer chains
- Negative
  - UV radiation links polymer chains
  - Tendency to shrink critical dimensions

Photoresist

- Though there are differences, all photoresists have the same basic chemical components
  - Polymers
  - Sensitizers
  - Additives

What Is a Polymer?

- A polymer is a large form (bulk) of collected monomers, which are individual repeating molecular chains
- Can be either natural, like protein, or synthetic, like plastic

What Is a Sensitizer?

- The sensitizer is the photoactive chemical in the resist material that reacts in response to radiant energy in the form of light

What Is an Additive?

- Additives are chemicals used modify specific chemical or light response aspects of the resist
  - These may include dyes to control reflectivity

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Negative Resists

- In negative resist, UV light causes the polymers to bond (polymerize) and form a material that is etch-resistant
- The polymers in most negative resists are of the **polyisoprene** type
- Polyisoprene is natural latex derived from the Para rubber tree. Generally for lithography applications, polyisoprene is made synthetically.
- Historically, negative resists were associated with health risks and have a tendency to shrink pattern feature sizes
- Modern chemistries in negative resists are safer and their adhesion properties superior

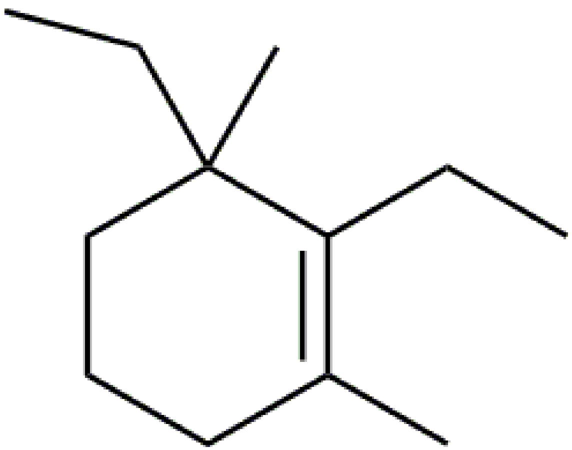
Negative Resists

- Small amounts of developer are required to develop negative resists because the resist is soluble before UV exposure.
- Organic developers solutions containing xylene are often used.
- Alcohols are then used to rinse away any partial cross-linked resist pieces and stop any developer that may still be working.
- A DI water rinse followed by a nitrogen dry ends the process

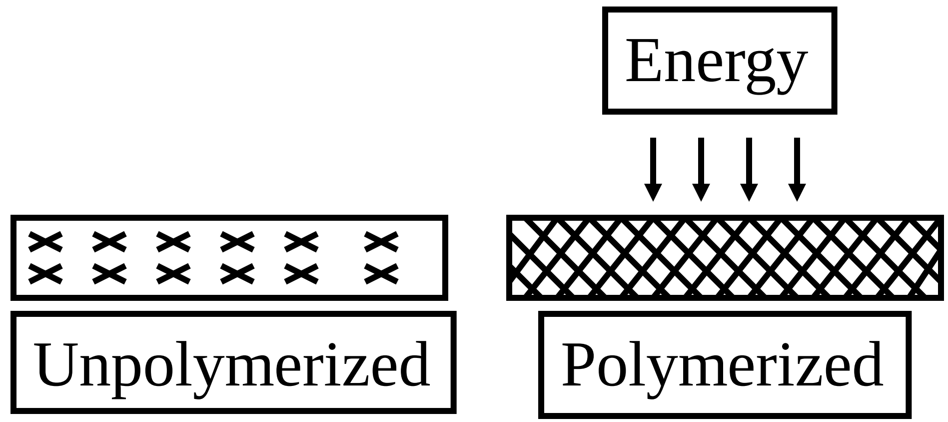
Negative Resists

- Swelling of the cross-linked regions during development is a problem associated with negative resists.
- As the resist absorbs the developer, features become distorted and jagged.
- This problem makes negative resists generally undesirable for features below 2 microns.
- Advances in negative resist chemistries may someday make sub micron features possible.

Negative Resist Chemistry



Polyisoprene monomer



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Positive Resists

- In positive resist, UV light causes bonded polymers to break, making them soluble in developer in a process known as **photosolubilization**
  - “What shows, goes!”
- Two general types of positive resists are widely used
  - Diazonaphthoquinone i-line Resists (DNQ)
  - Chemically Amplified Deep Ultraviolet Resists (DUV)

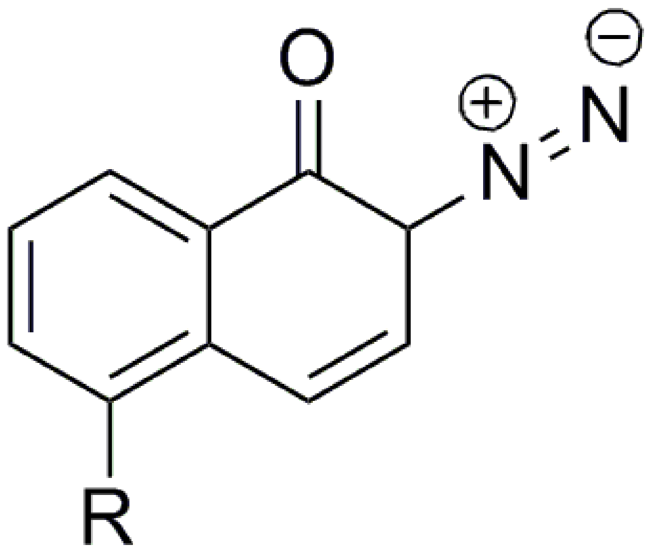
DNQ Resists

- DNQ is a photoactive compound (PAC)
- Before UV light exposure DNQ prevents degradation of the resist
- After UV light exposure DNQ rapidly degrades allowing the novolak resin to become soluble in developer
- Typically exposed at 365nm (i-line)

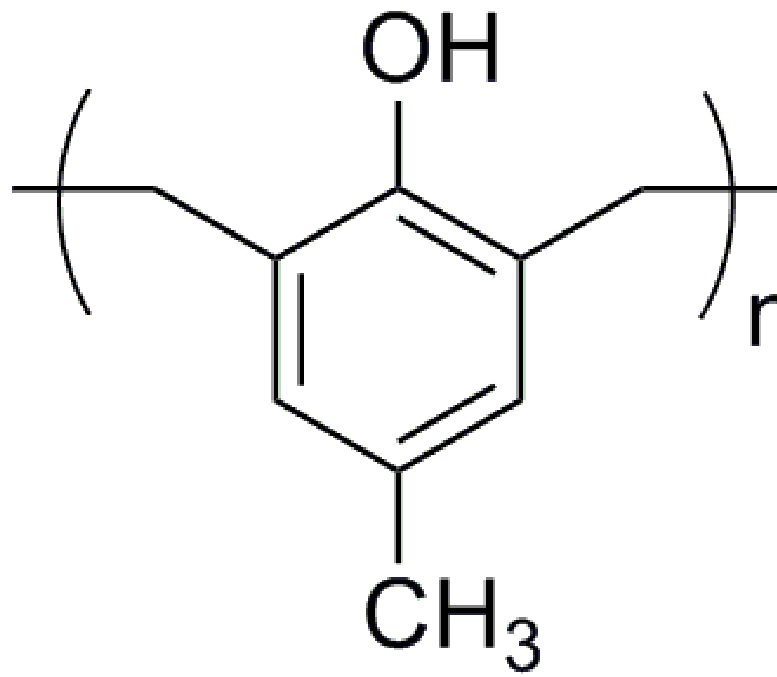
DNQ Resists

- The polymer in DNQ resist is the phenol-formaldehyde polymer, also called phenol-formaldehyde novalak resin
- Phenol-formaldehyde polymer, was first formed as bakelite. It is formed by an elimination reaction of phenol with formaldehyde. Phenol formaldehyde resins, as a group, are formed by a reaction which may be either acid or base catalyzed.
- Commonly used when non-critical features down to 0.35 microns are desirable
- Novalac is a common glue used to bind layers of plywood

Positive Resist Chemistry



Common Photoactive Compound
of Diazonaphthoquinone (DNQ)



Basic Aromatic Ring of Novolak Polymer

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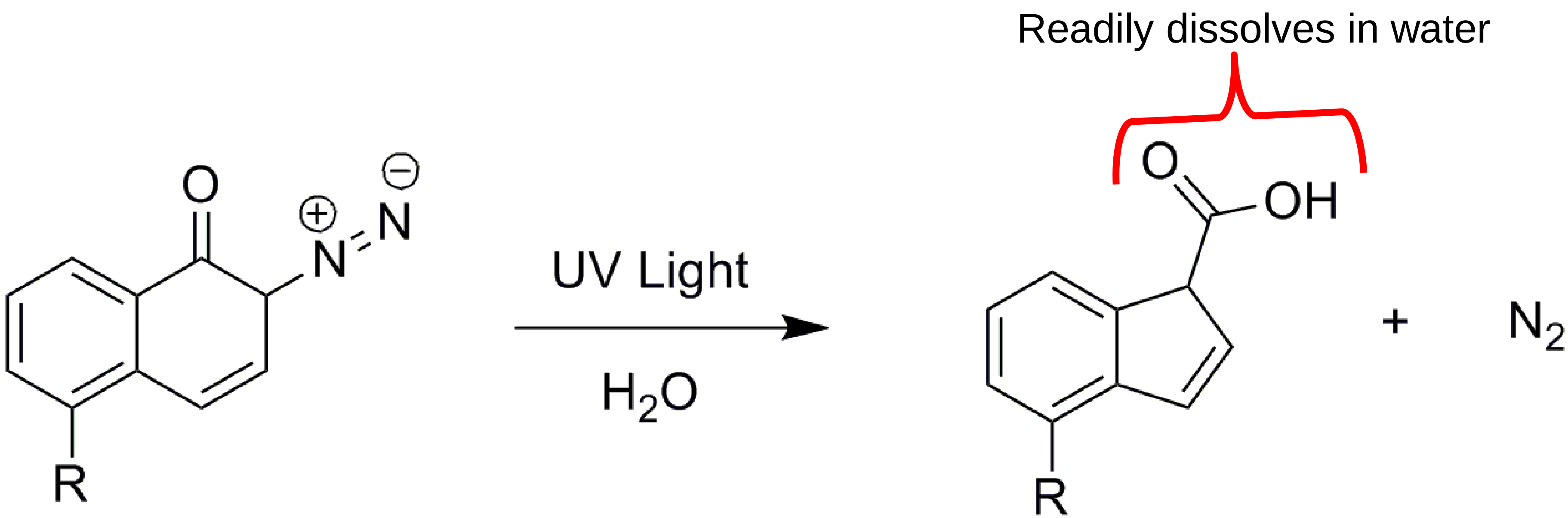
Reaction of Positive DNQ After UV Light Exposure



Photoactive compound

Dissolution enhancer

Chemically Amplified DUV Resists

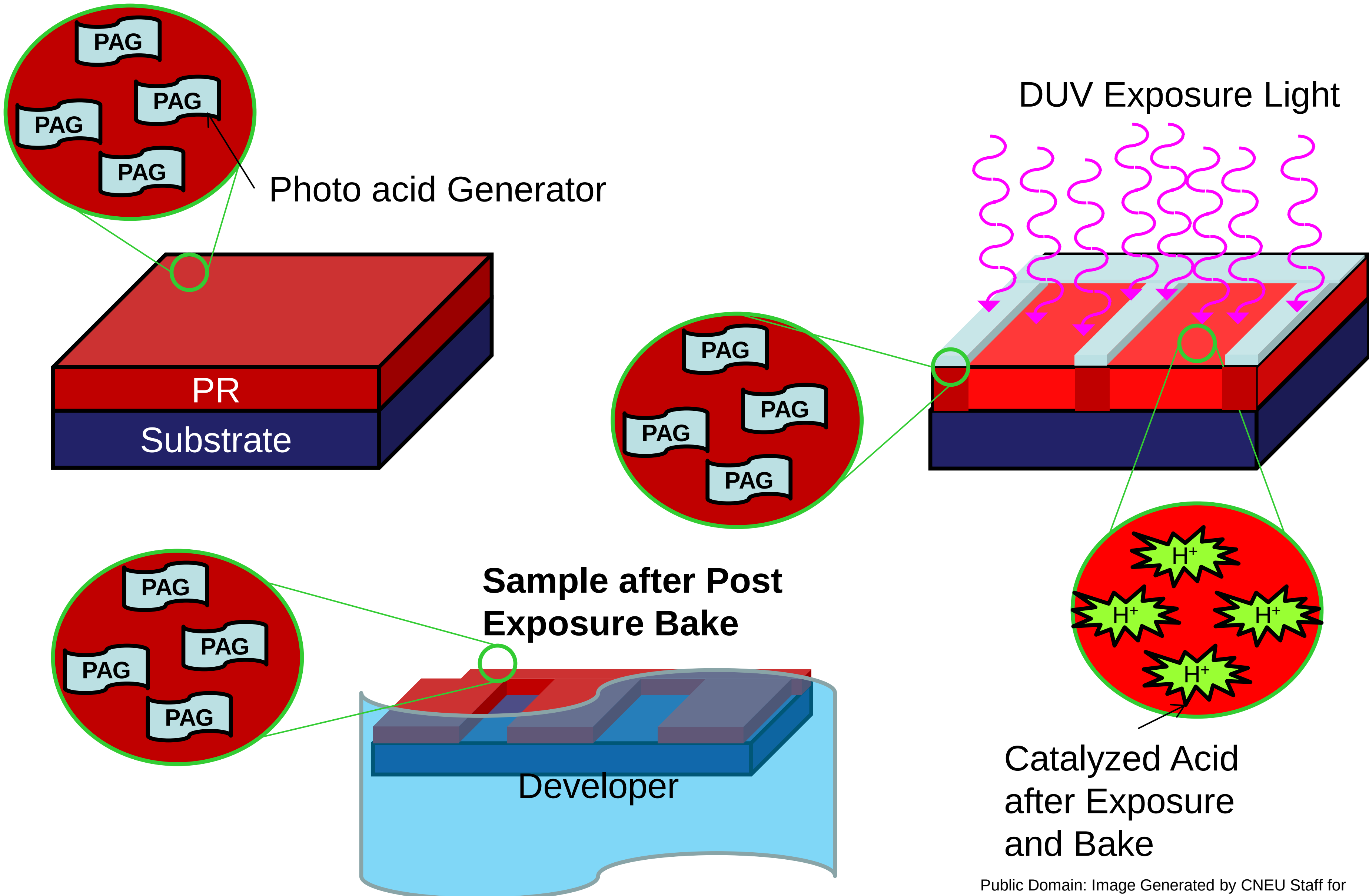
- DUV resists use a sensitizer known as a photo acid generator (PAG)
- Acids are produced in the exposed areas of the resist
- The acid then removes a protecting group from the resist during the post-exposure bake
- The exposed areas then become soluble in developer

Quirk, M. Serda, J. *Semiconductor Manufacturing Technology*. Prentice Hall. New Jersey 2001

Chemically Amplified DUV Resists

- CA resists have a high sensitivity for DUV lithography due to a unique catalytic reaction that occurs in the resist
- The resist, poly(4-hydroxystyrene), or (PHS), is formulated with a resin (t-BOC) that renders resist insoluble and an onium salt that produces an acid upon exposure to deep UV
- The acid removes t-BOC from the resist molecules during a post exposure bake making the PHS soluble in developer

Chemically Amplified DUV Resists



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Chemically Amplified DUV Resists

- The polymer in DUV resists is poly-parahydroxystyrene (PHS)
- Commonly used when sub 0.25 micron features are desirable
- Typically exposed at 248 nm or 193 nm

Quirk, M. Serda, J. *Semiconductor Manufacturing Technology*. Prentice Hall. New Jersey 2001

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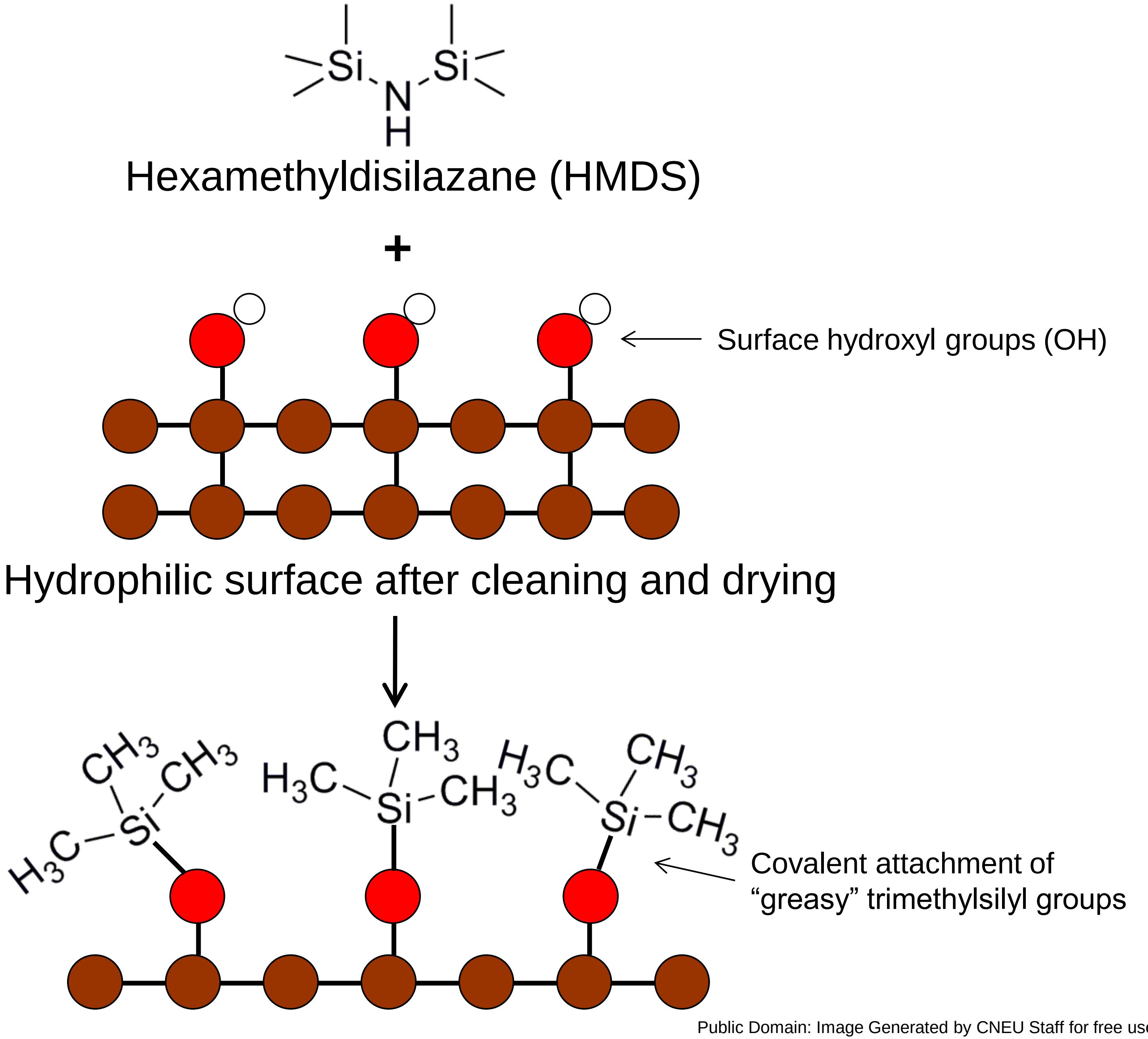
Hexamethyldisilazane (HMDS)

- Hexamethyldisilazane (HMDS) is used as a **primer**.
  - This chemical promotes the adhesion of photoresist, by displacing any water left behind on the substrate's surface after the dehydration bake, and reduces surface tension.
  - HMDS *primes* the substrate's surface by adding an organic layer (hydrocarbons) to which photoresist, being mainly organic, can easily attach.



Hydrophobic surface after priming with HMDS

HMDS Application

- Industry utilizes several techniques for applying HMDS efficiently
  - Immersion priming
  - Spin priming
  - Vapor priming

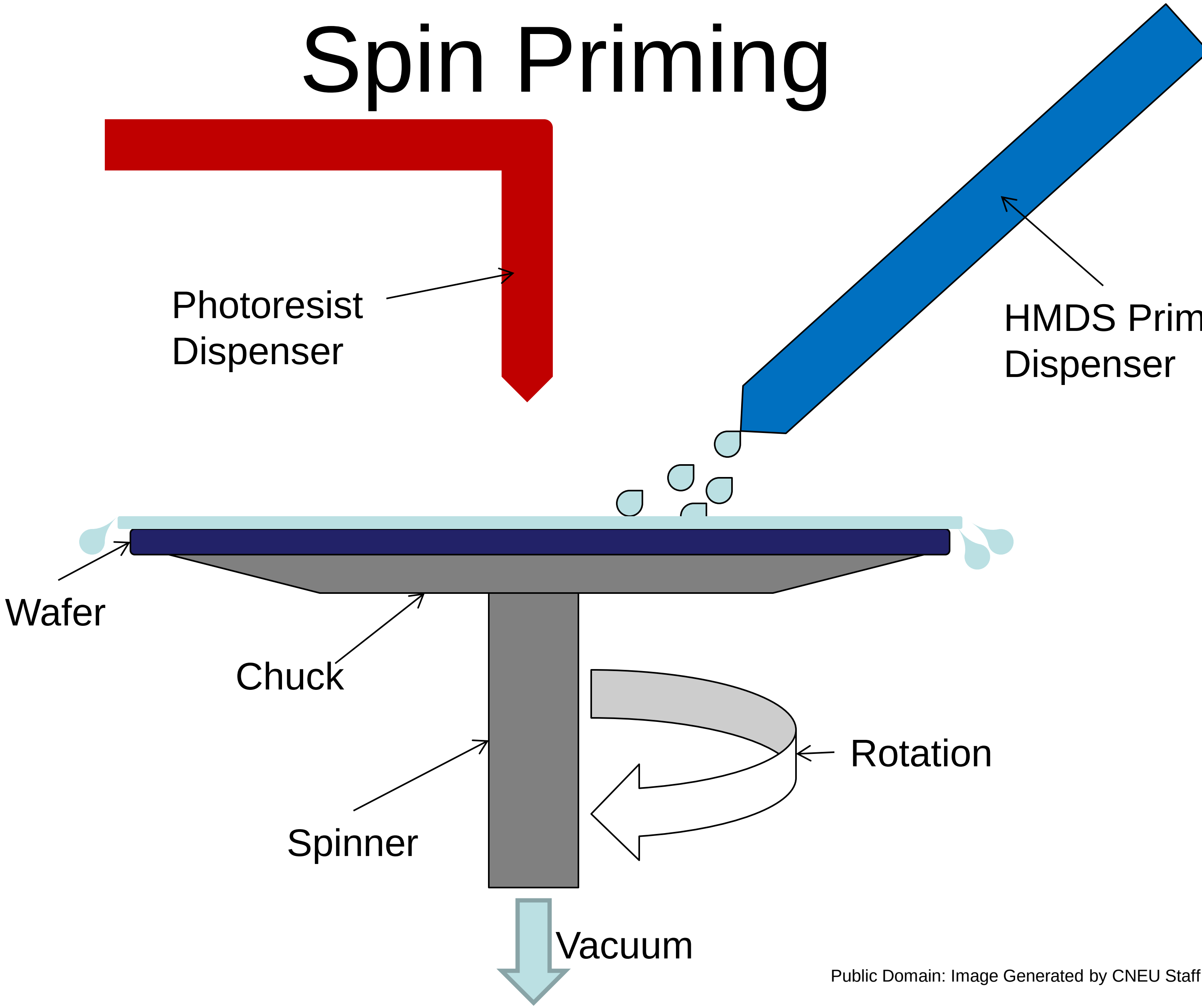
Immersion Priming

- This is the easiest method of primer application
- Immersion priming is accomplished by simply dipping the substrate in a beaker of liquid
- Immersion priming has the drawbacks of:
  - Being a manual method
  - Exposing the substrate to contamination

Spin Priming

- This is the most common method of applying primer
- HMDS is applied to the substrate while it is on the resist spinner
  - Primers can be dispensed manually from a syringe or automatically
- Automatic spinners have a separate system to dispense HMDS just before application of the resist
- Spin priming takes place in-line with the resist step, a major advantage

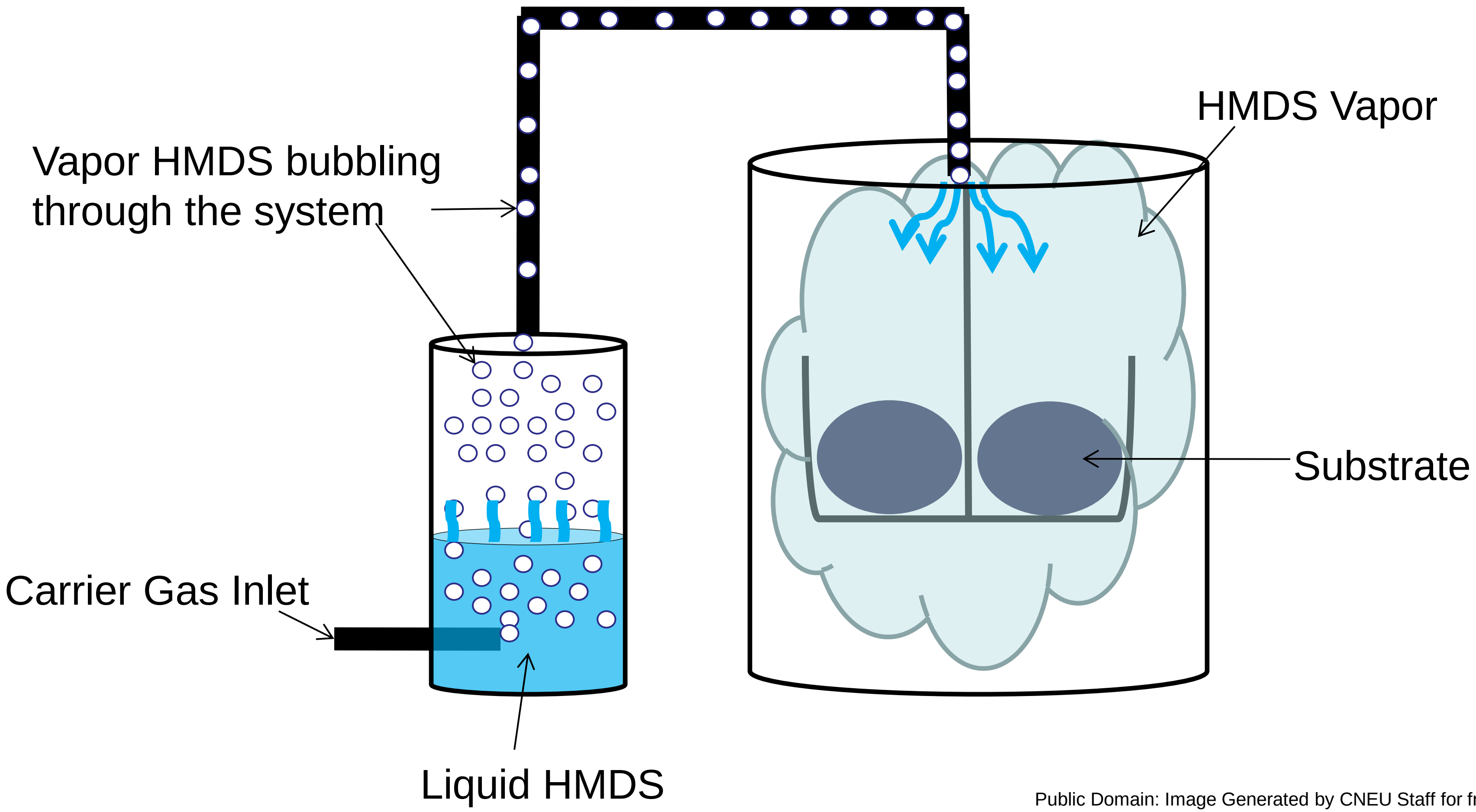
Spin Priming



Vapor Priming

- This priming method uses HMDS in vapor form, limiting substrate contamination, reducing cost, and eliminating the damage liquid HMDS can do to photoresist
- HMDS is piped into a chamber holding the substrate where they are completely coated
- HMDS vaporization can be done by bubbling nitrogen through the HMDS, heating the HMDS or dispensing HMDS under vacuum

Vapor Priming



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Resist Application

- There are several methods for applying resist
  - Static spin
  - Dynamic dispense
  - Moving-arm dispensing
  - Automatic spinners

Static Spin

- The substrate is placed on a vacuum chuck, several cubic centimeters of resist are placed in the center of the substrate and allowed to reach a desired diameter
- The chuck then spins, spreading the resist and spinning off the excess

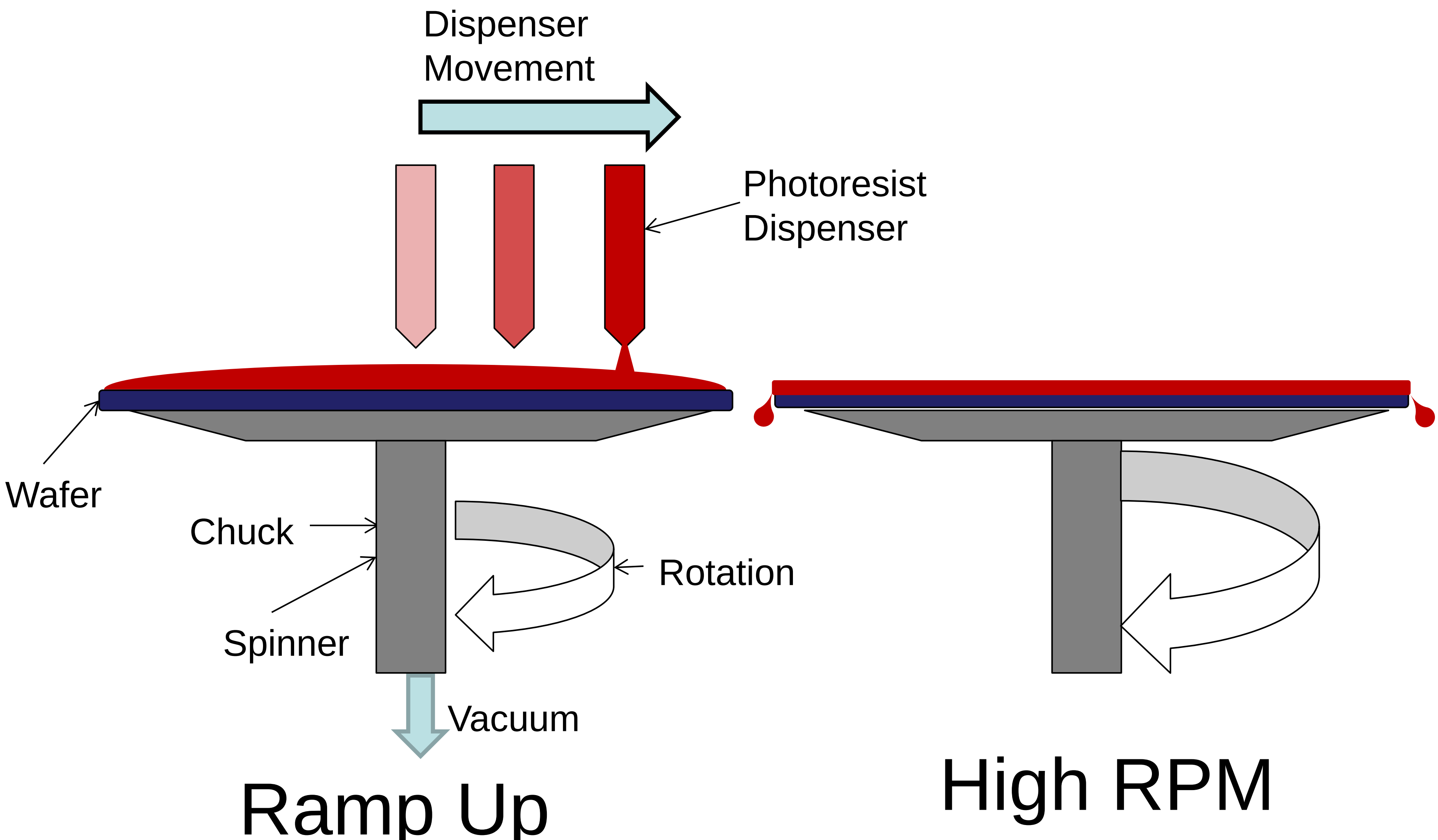
Dynamic Dispense

- The substrate rotates at a low speed (500 rpm) while the resist is applied
- After the resist covers the substrate, the spinner is accelerated to a high speed to achieve uniformity and thickness requirements
- This method conserves resist and increases uniformity

Moving-arm Dispenser

- This method proceeds in a similar fashion as the dynamic dispense method except that the dispenser is an arm that moves across the substrate surface from the center out, increasing uniformity

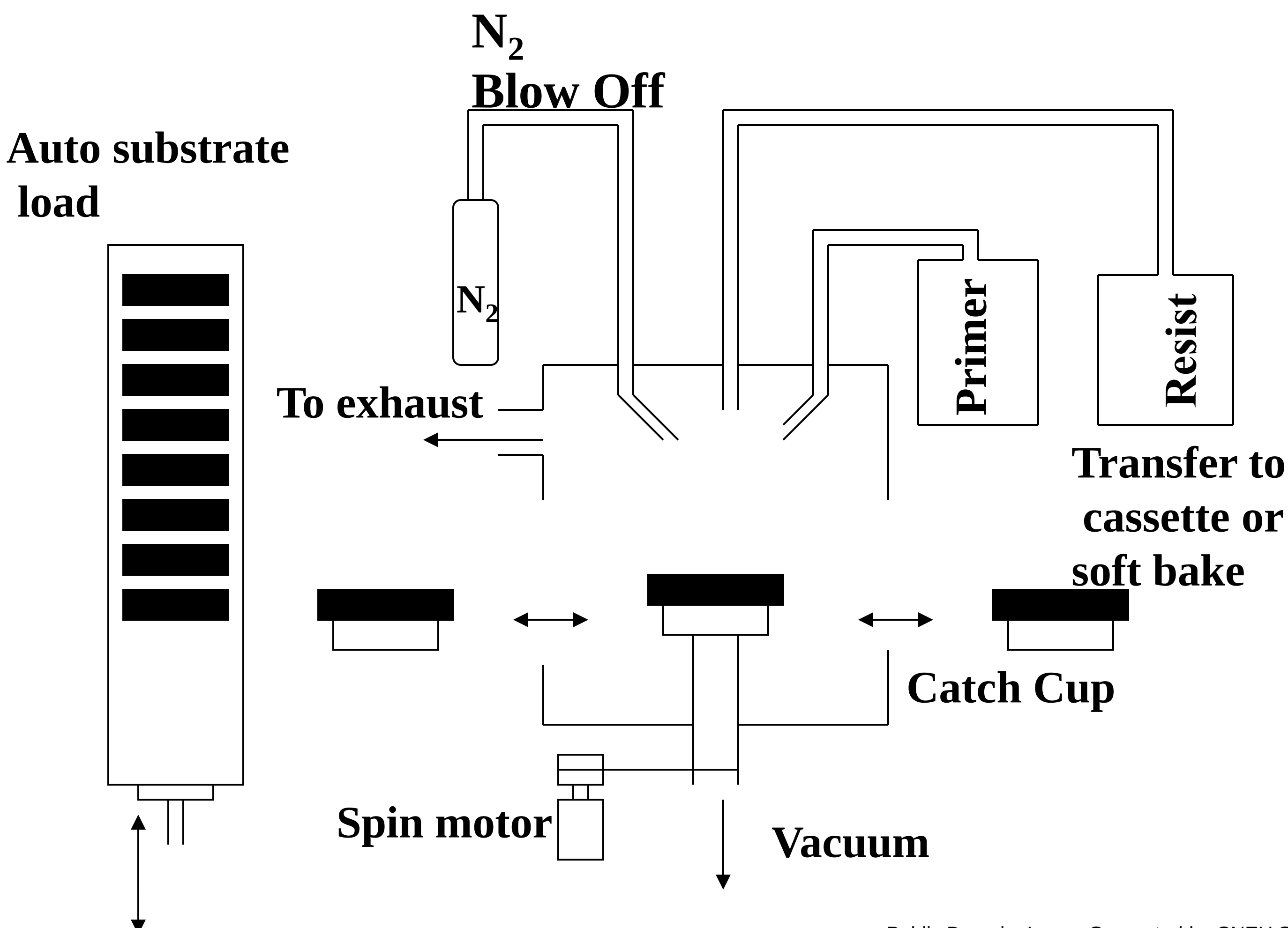
Moving-arm Dispenser



Automatic Spinners

- Automatic spinners combine the following steps
  - Primer application
  - Resist dispense and spin
  - Soft bake

Automatic Spinner



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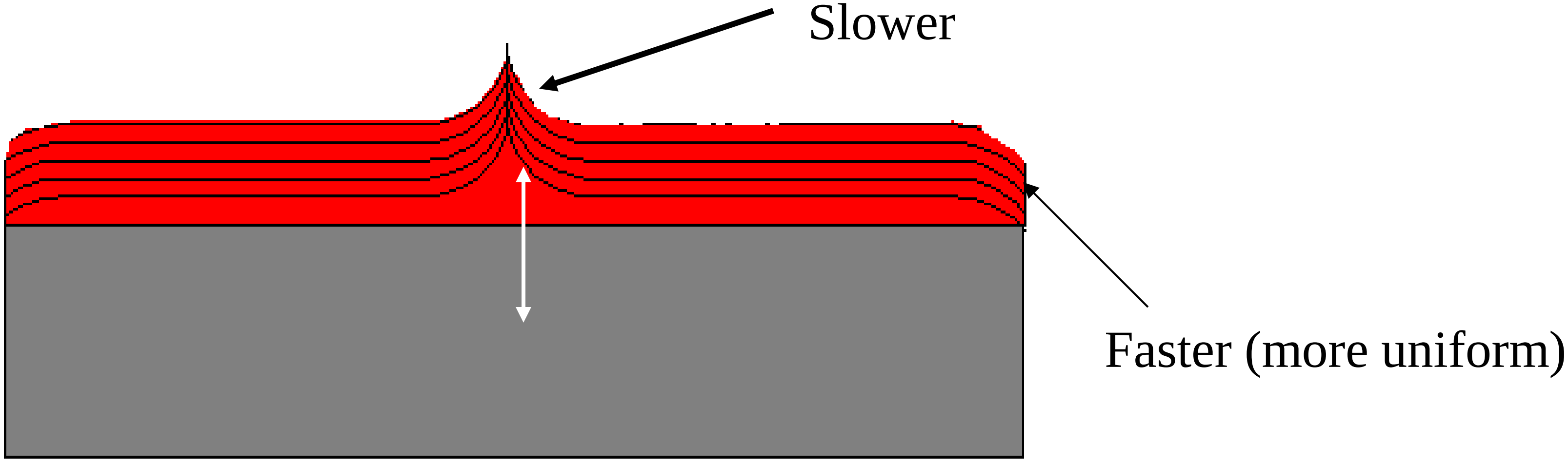
Spin-on Photoresist

- The following are crucial factors to insure proper resist application
  - Time
  - Spin speed
  - Acceleration rate
  - Resist adhesion quality

Advanced Lithography Basics

- Photoresist spins
  - Spin speed impacts uniformity



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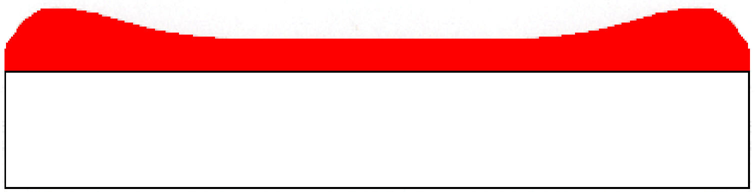
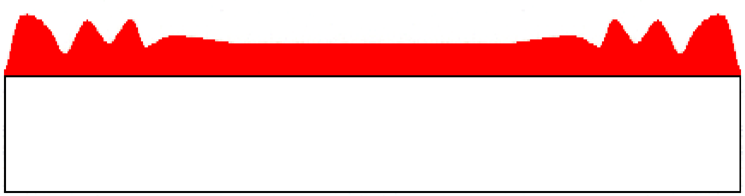
Stages of Resist Coating

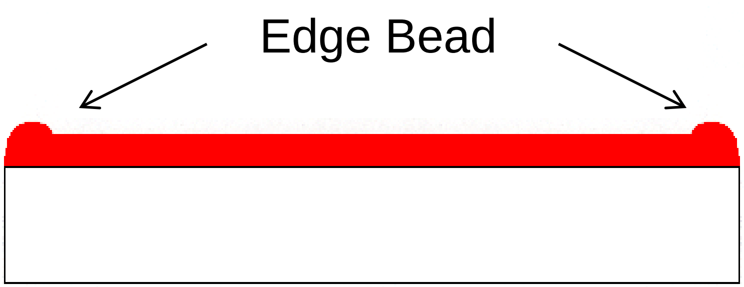
1. Equilibrium Stage
(stopped)



2. Wave Formation Stage
(~2 revolutions)



3. Corona Stage
(~30 revolutions)



4. Spiral Stage
(~1000 revolutions)

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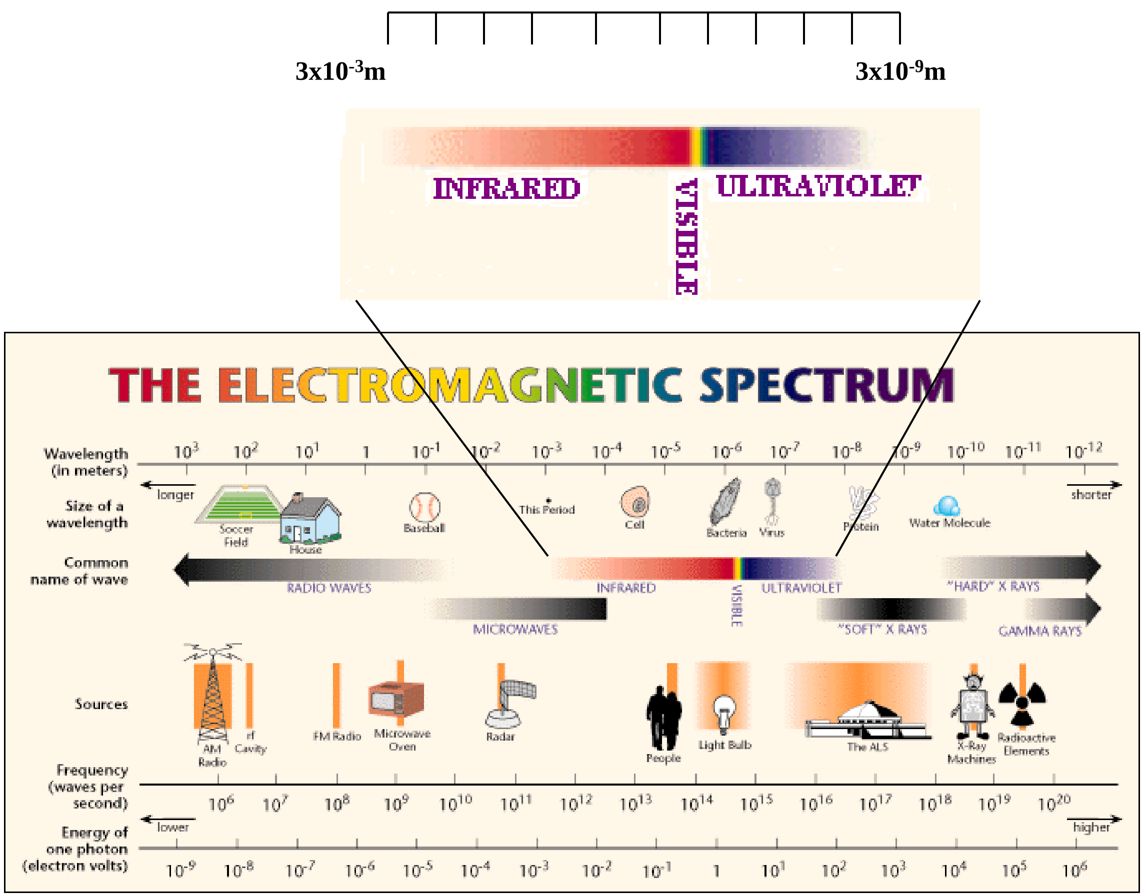
The Electromagnetic Spectrum

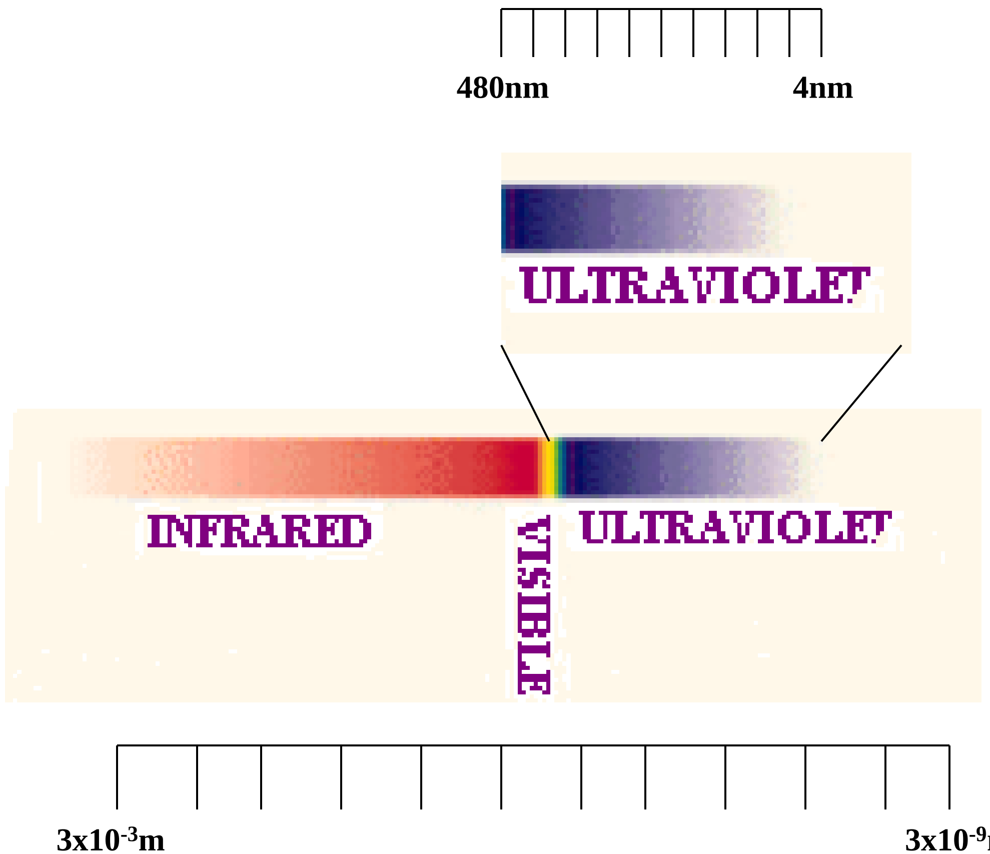
- The spectrum is organized by wavelength size
  - Radio waves are among the longest
  - Gamma rays are among the shortest

Wavelengths of Interest in Nanofabrication



Adapted from: Swapon Chattopadhyay, Ranjan Ray, David Friedberg, and LaurenOsofsky. US U.S.Department of Energy. http://bc1.lbl.gov/CBP_pages/educational/WoB/index1.htm

Wavelengths of Interest in Photolithography



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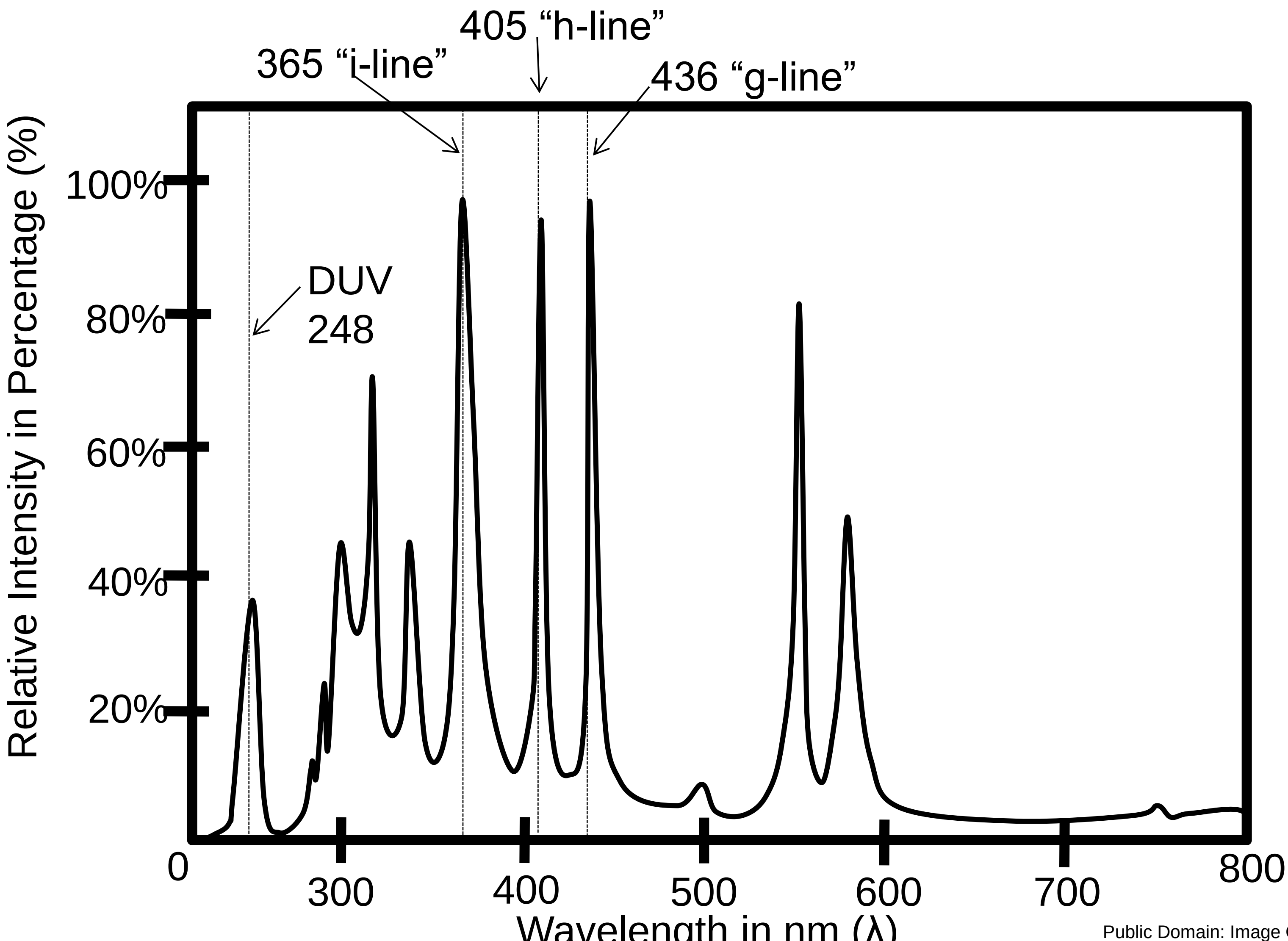
Specific UV Wavelengths

- Conventional photoresists for contact lithography (like the ones we use) are sensitive to one of three major peaks in the UV spectrum
  - 436 nm (g-line)
  - 405 nm (h-line)
  - 365 nm (i-line)
- High pressure mercury vapor lamps are used as the radiation source

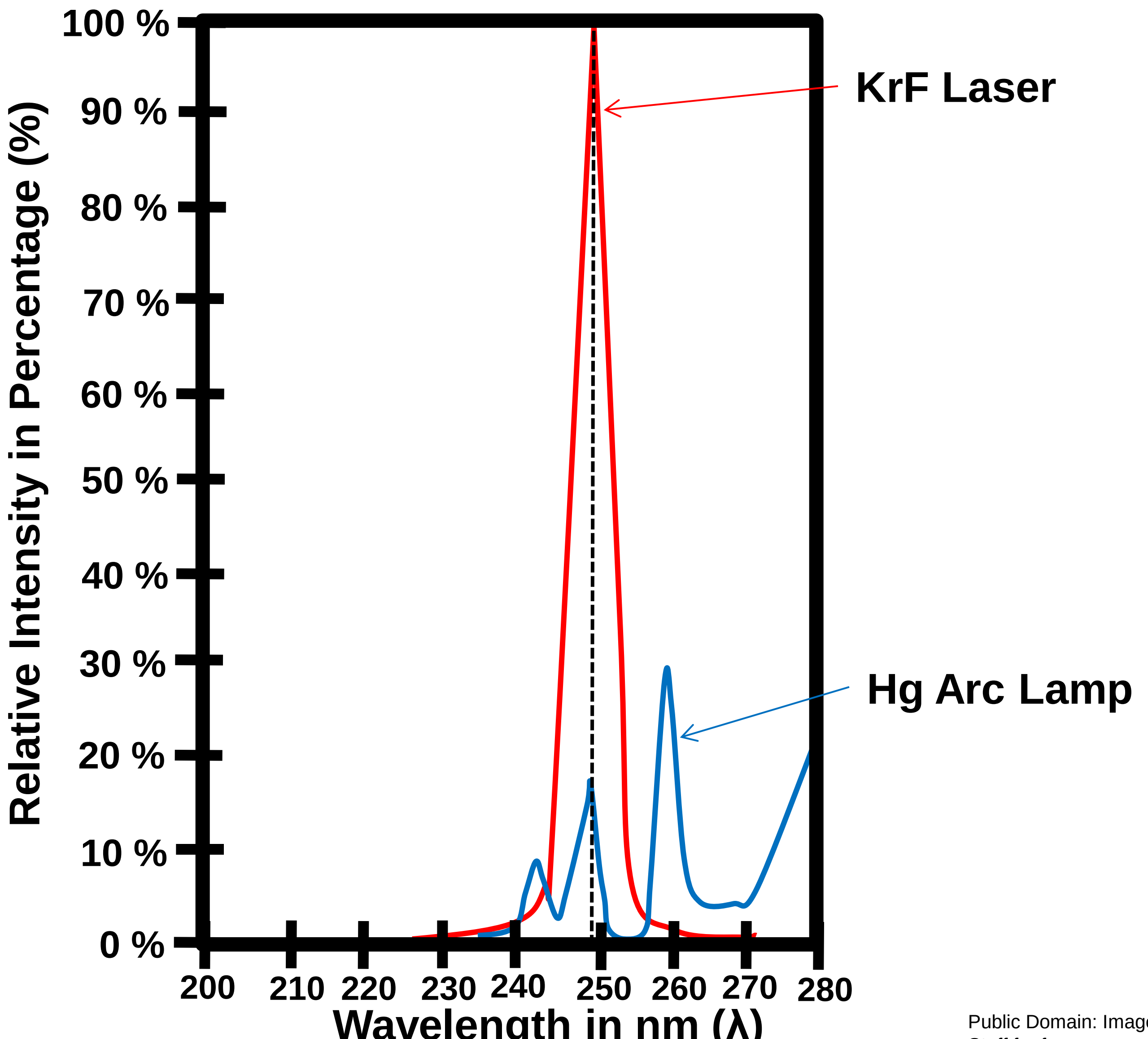
Emission Spectrum of High Intensity Mercury Lamp



Excimer Lasers Emit the Most Intense Deep Ultra Violet Radiation

Laser source	**Wavelength (nm)**
XeF	351
XeCl	308
KrF	248
ArF	193

Spectral Emission Intensity of 248 nm Excimer Laser vs. Mercury Lamp



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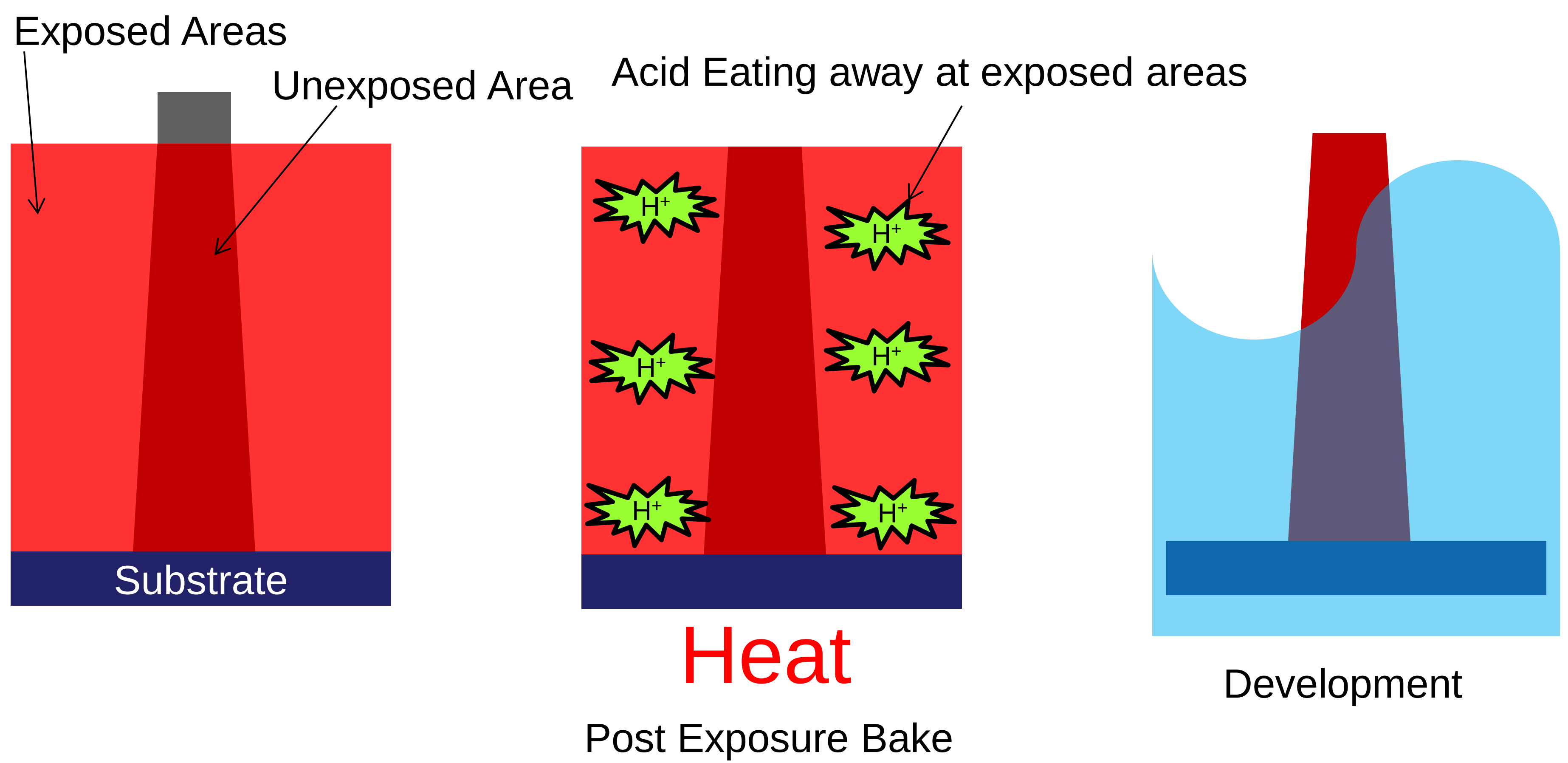
Post Exposure Bake

- DUV resists
  - Post Exposure Bake (PEB) catalyzes critical chemical reactions in DUV resists
  - During exposure, the UV light generates an acid in the exposed regions.
  - PEB catalyzes the acid mediated reactions that cause the exposed regions to become soluble in developer
  - Time and temperature for a post-exposure bake is as critical as exposure and development time.

Post Exposure Bake

- DUV resists continued
  - Temperatures are controlled within 0.1^{o}C to prevent critical dimension degradation.
  - PEB are typically 10-15^{o}C higher than soft bakes
  - Amine contamination will neutralize the effects of acidification in the exposed areas.
  - Advances in some DUV resists permit a 30 minute delay time until amine contamination neutralizes the acids. However immediate development will minimize inhibition reactions

Acid Catalyzed Reaction of DUV



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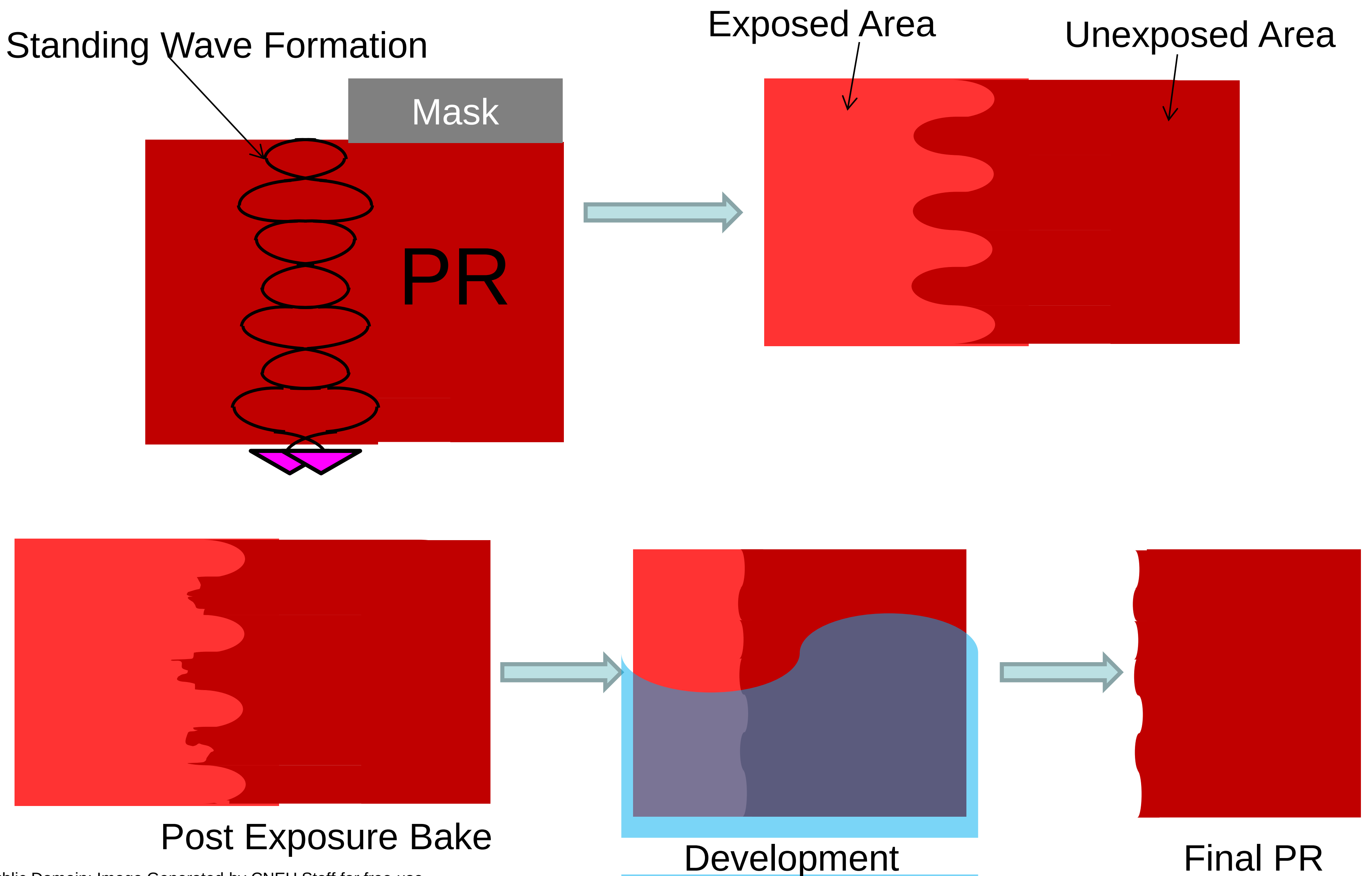
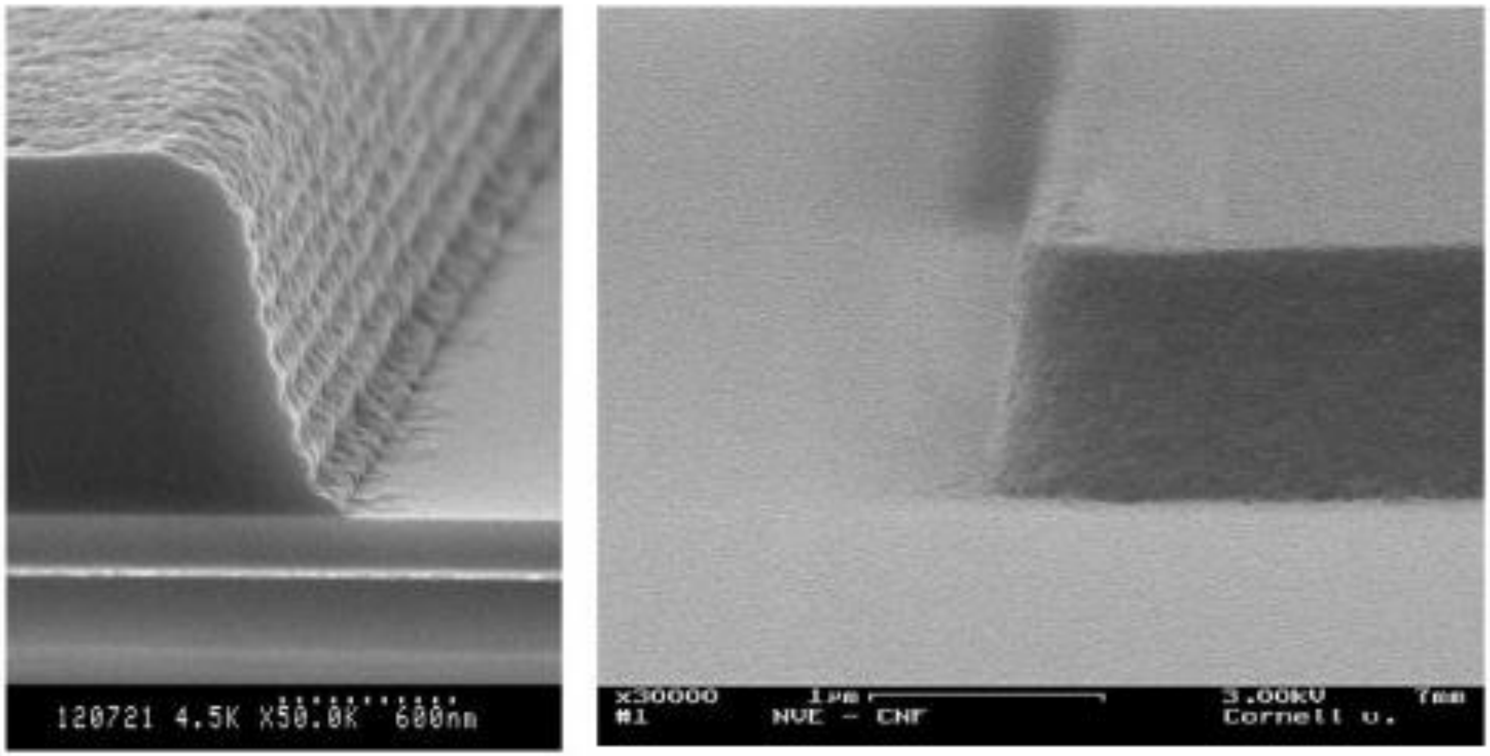
Post Exposure Bake

- Conventional positive i-line resists
  - Improves resist adhesion to substrate
  - Drives off solvents in the resist
  - PEB reduces standing waves for positive i-line resists

PEB Reduction of Standing Wave Effects



PEB Reduction of Standing Wave Effects



Shipley 1813 no PEB

Shipley 1813 115°C 60 sec. PEB

Cornell Nano Scale Science and Technology Facility

Post Exposure Bake

- Conventional negative i-line resists
  - Hardens cross-linked polymers in exposed areas
  - Prevents desired features from being degraded during development

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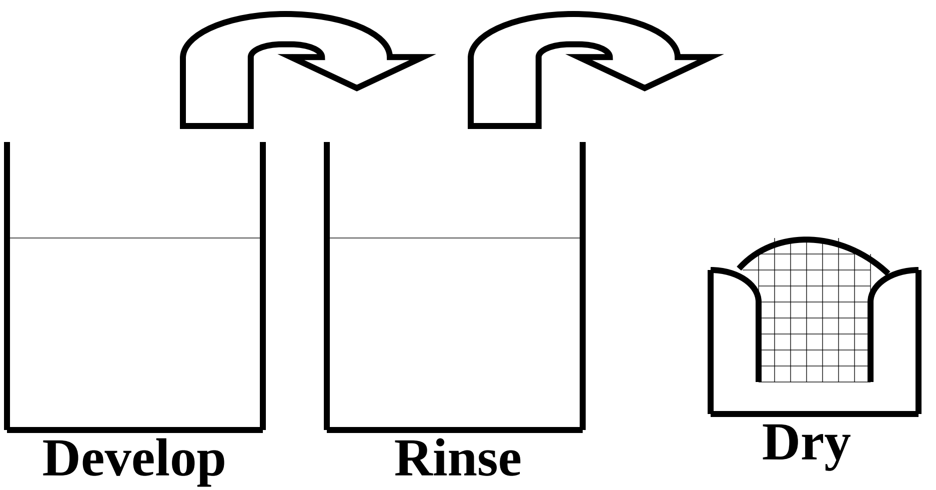
Development

- There are three major methods of development:
  - Immersion
  - Spray development
  - Puddle development

Immersion

- The substrate is simply immersed in a development tank for a specific amount of time before being transferred to a rinse tank



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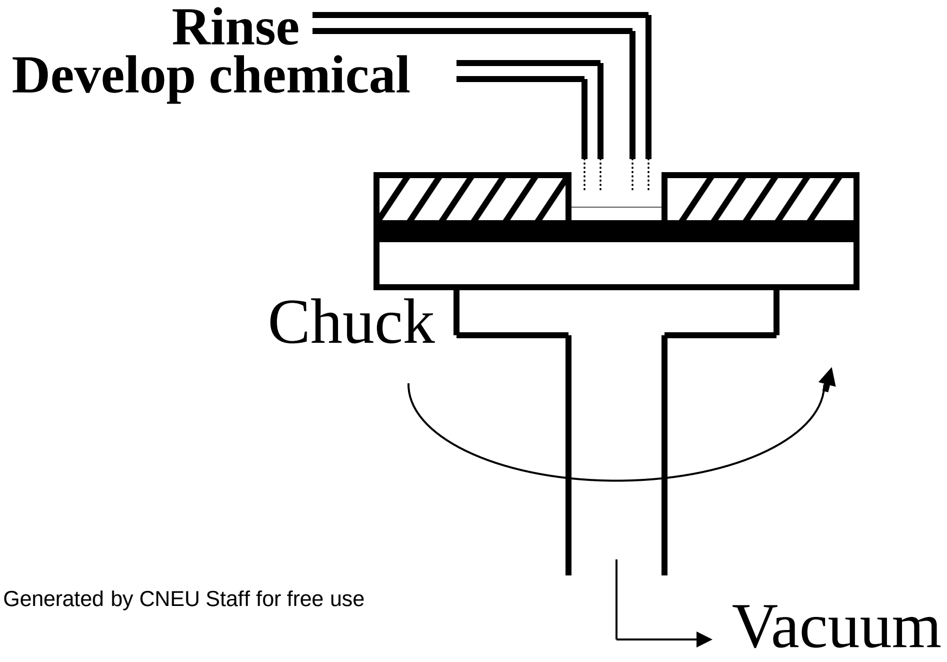
Spray Development

- A substrate is place on a vacuum chuck and spun while developer and rinse are sprayed onto the substrate surface



Puddle Development

- The substrate is placed on a chuck and developer is sprayed onto the surface until a puddle forms and remains until the resist is developed
- The chuck spins and the substrate is rinsed and dried

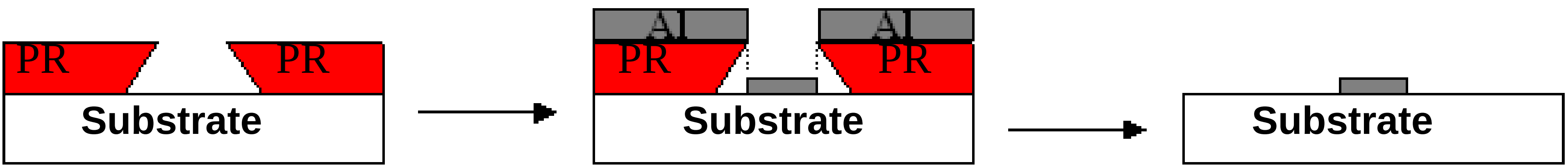
Liftoff

- Liftoff is an additive process
- It uses a sacrificial PR layer and a metal deposition as an additive process
- Metal layer is deposited with an evaporator, plasmas can cause contamination

Scenario One: Sidewalls Slant Inward

- This profile is desirable for deposition processes, such as evaporation and the selective removal of unwanted material in a process known as **liftoff**

The Liftoff Process



Sidewalls slant inward
(acts like a roof)

Evaporation:
deposit aluminum

Acetone strips
photoresist and
unwanted aluminum

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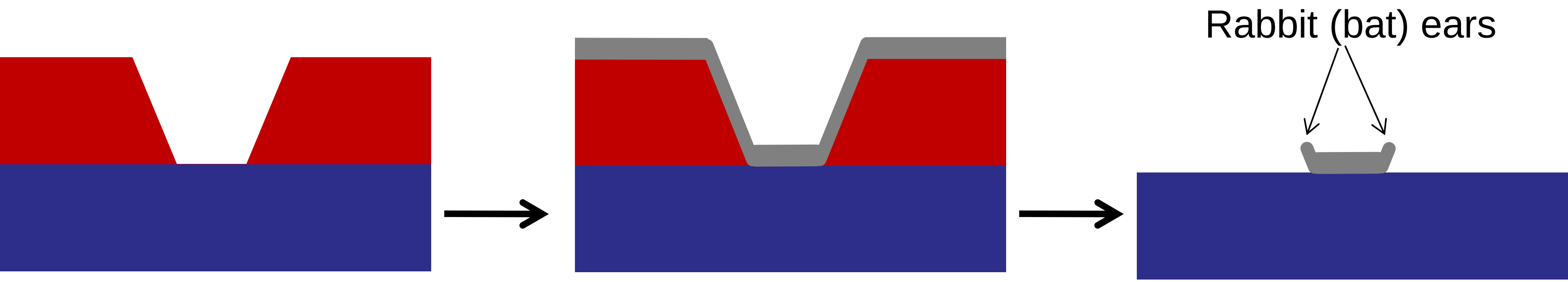
Scenario Two: Sidewalls Slant Outward

- Sidewall slant out, rabbit ears and metal tearing, not desirable



Sidewalls slant inwards

Evaporation: deposit Al into pattern including the side walls of the trench

Acetone strips of the PR and most of the unwanted Al, but some Al remains at the edges of the feature

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