# *ChemE 2200 – Chemical Kinetics Lecture 11*

*Today*: Photochemical Chain Reactions, cont'd.

Isotopic Separation

Photolithography *"A resist resists what?"*

*Recap*: (see Handout)

The Ozone Cycle

*Converts UV photons into Heat*

| | |
|---|---|
| $O_2 + \text{UV photon} \rightarrow \cdot O \cdot + \cdot O \cdot$ | initiation |
| $\cdot O \cdot + O_2 + M_{cold} \xrightarrow{k_2} O_3 + M_{hot}$ | propagation |
| $O_3 + \text{UV photon} \rightarrow O_2 + \cdot O \cdot$ | propagation |
| $\cdot O \cdot + O_3 \xrightarrow{k_4} 2O_2$ | termination |

overall reaction: $M_{cold} + \text{UV photon} \rightarrow M_{hot}$

The Chlorofluorocarbon (CFC) Cycle

*Consumes propagators of the Ozone Cycle*

| | | |
|---|---|---|
| | $CF_2Cl_2 + \text{UV photon} \rightarrow \cdot CF_2Cl + \cdot Cl$ | initiation |
| inhibition of the ozone cycle | $\cdot Cl + O_3 \xrightarrow{k_2} \cdot ClO + O_2$ | propagation |
| inhibition of the ozone cycle | $\cdot ClO + \cdot O \cdot \xrightarrow{k_3} \cdot Cl + O_2$ | propagation |
| | $\cdot Cl + CH_4 \xrightarrow{k_4} HCl + \cdot CH_3$ | inhibition (of the CFC cycle) |

Overall reaction: $\cdot O \cdot + O_3 \rightarrow 2O_2$

Photon energies required to dissociate simple molecules

| reaction | photon energy eV | kJ/mol | wavelength nm |
|---|---|---|---|
| $H_2 + h\nu \rightarrow H(1s) + H^*(2p)$ | >14.7 | >1400 | <85 |
| $O_2 + h\nu \rightarrow O(^3P) + O^*(^1D)$ | 7.0 | 670 | 175 |
| $Cl_2 + h\nu \rightarrow Cl + Cl^*$ | 2.6 | 250 | 480 |
| $Br_2 + h\nu \rightarrow Br + Br^*$ | 2.4 | 230 | 510 |
| $I_2 + h\nu \rightarrow I(^2P_{3/2}) + I^*(^2P_{1/2})$ | 2.5 | 240 | 500 |
| $HI + h\nu \rightarrow H + I$ | 3.8 | 365 | 330 |
| $NO_2 + h\nu \rightarrow NO + O$ | 3.4 | 325 | 365 |
| $NH_3 + h\nu \rightarrow NH_2 + H$ | 5.6 | 540 | 220 |
| $H_2O + h\nu \rightarrow H + OH$ | 5.1 | 490 | 240 |
| $R-C(O)H + h\nu \rightarrow R + C(O)H$ | 3.8 | 365 | 330 |
| $R-C(O)R + h\nu \rightarrow R + C(O)R$ | 3.8 | 365 | 330 |

1 eV/molecule = 96 kJ/mol

1 eV/molecule = 1240/$\lambda$ (nm)

# Photons for Selective Reactions

Thermal Chemistry: heat reactants $\Rightarrow$ increase kinetic energy $\Rightarrow$ break bonds indiscriminately

*Effective but not elegant. Like using a hammer to disassemble a molecule.*

Photochemistry: tune photon energy to break bonds strategically

*Effective and elegant. Like using a scalpel to dissect a molecule.*

But laser photons are expensive: ~$100/mol. cf. molecules: ~$0.01 to $1/mol.

*Photon reactants must be justified by high selectivity and/or high yield.*

Isotopic Separation: $^{1}H/^{2}H$, $^{6}Li/^{7}Li$, $^{12}C/^{13}C$, $^{16}O/^{18}O$, $^{235}U/^{238}U$

*Isotopic separation for medicine, chemical and biochemical research, and atomic power is one of ChemE's Top Ten Achievements for its first 75 years.*

How to separate $^{35}Cl$ (76% natural abundance) from $^{37}Cl$ (24%)?

Distill a mixture of $^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$? Not economically feasible.

Distill a mixture of $H^{35}Cl$ and $H^{37}Cl$? Not economically feasible.

*Use photochemistry to selectively react molecules with a specific isotope.*

# Photochemistry for Isotopic Separation of $^{35}Cl$ and $^{37}Cl$

*Strategy*

Convert $Cl_2$ to ICl: $Cl_2 + I_2 \rightarrow ICl$ Separate ICl from $Cl_2$ and $I_2$.

b.p. = –34ºC 184ºC 97ºC

Selectively dissociate $I^{35}Cl$:

$I^{35}Cl + h\nu \rightarrow {}^{35}Cl\cdot + I\cdot$

$I^{37}Cl + h\nu \not\rightarrow$ (no rxn)

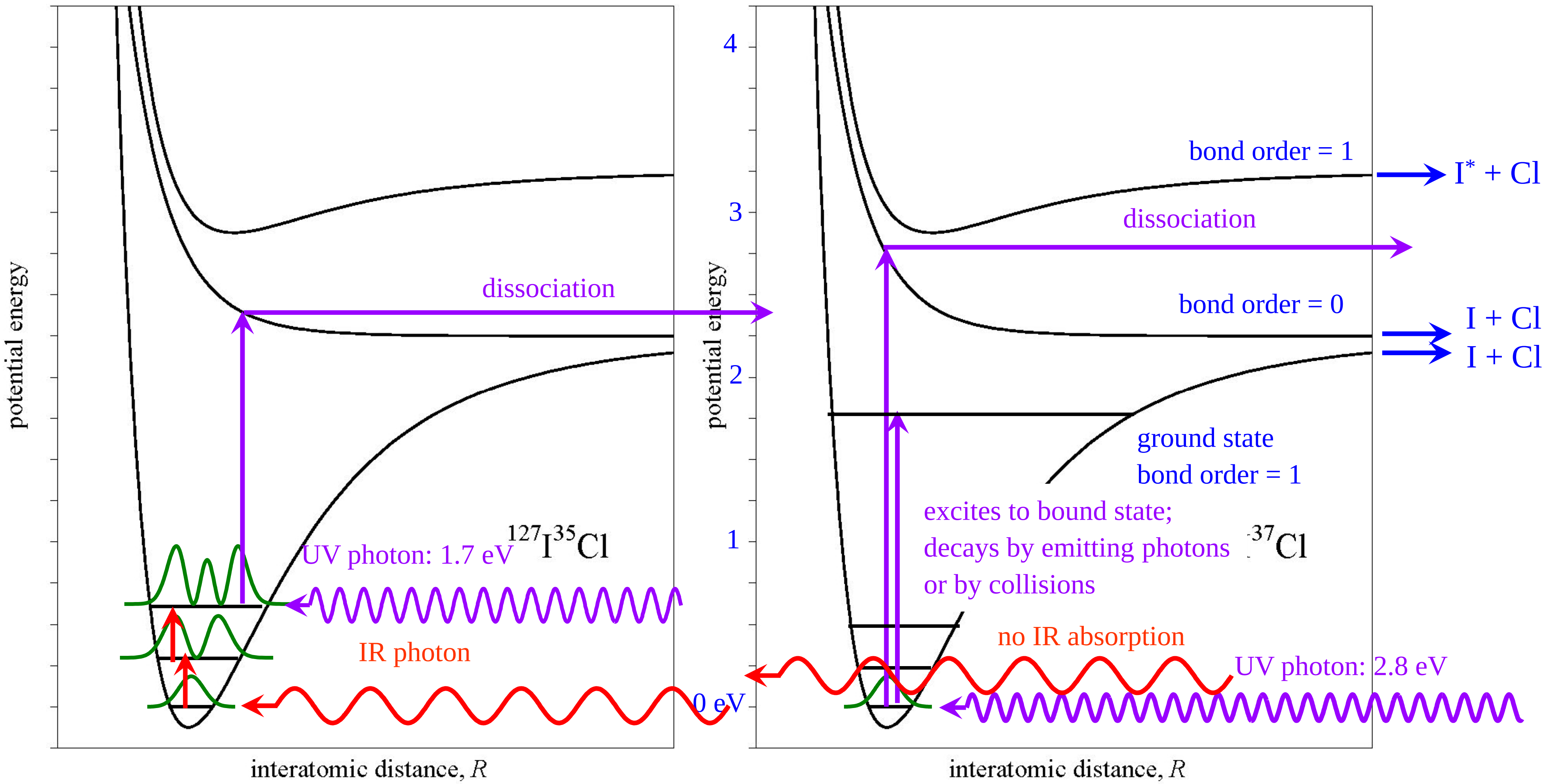
*How?*

${}^{35}Cl\cdot + CH_4 \rightarrow CH_3{}^{35}Cl + H\cdot$ Separate $CH_3Cl$ from $CH_4$, ICl, and $CH_3I$.

b.p. = –182ºC –24ºC

# Photochemistry for Isotopic Separation of $^{35}$Cl and $^{37}$Cl

Nuclear charges are the same ⇒ Identical potential energy curves.




How to dissociate ICl? Irradiate with UV photons with $E$ > 2.8 eV. Dissociates *both* I$^{35}$Cl and I$^{37}$Cl.

How to *selectively* dissociate I$^{35}$Cl? Irradiate with IR photons tuned to I$^{35}$Cl vibrational levels and irradiate with UV photos with $E$ ~ 1.7 eV.

# Photochemistry for Isotopic Separation of $^{35}Cl$ and $^{37}Cl$

*Strategy*

Convert $Cl_2$ to ICl: $Cl_2 + I_2 \rightarrow ICl$ Separate ICl from $Cl_2$ and $I_2$.

b.p. = –34°C 184°C 97°C

Selectively dissociate $I^{35}Cl$:

$$I^{35}Cl + h\nu \rightarrow {}^{35}Cl\cdot + I\cdot$$

$$I^{37}Cl + h\nu \not\rightarrow \text{(no rxn)}$$

*How?*

$$^{35}Cl\cdot + CH_4 \rightarrow CH_3{}^{35}Cl + H\cdot$$

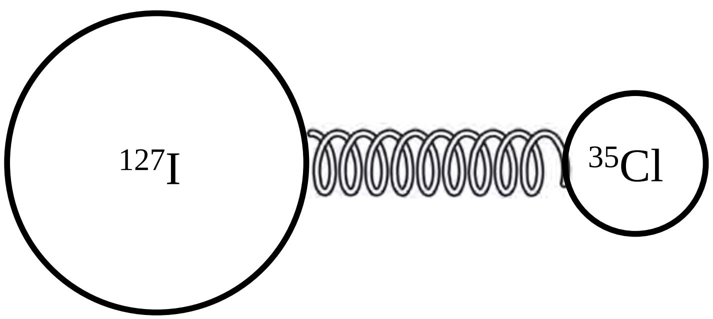
Separate $CH_3Cl$ from $CH_4$, ICl, and $CH_3I$.

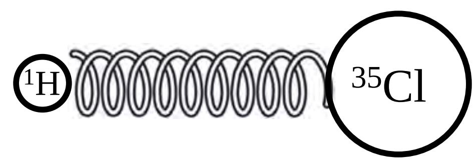
b.p. = –182°C –24°C

Irradiate with IR photons tuned to $I^{35}Cl$ vibrational levels; irradiate with UV photos with $E$ ~ 1.7 eV.

Why convert $Cl_2$ to ICl? Why not selectively irradiate $^{35}Cl^{35}Cl$? $Cl_2$ is not infrared-active.

Why not convert $Cl_2$ to HCl, which is a gas at 20°C?



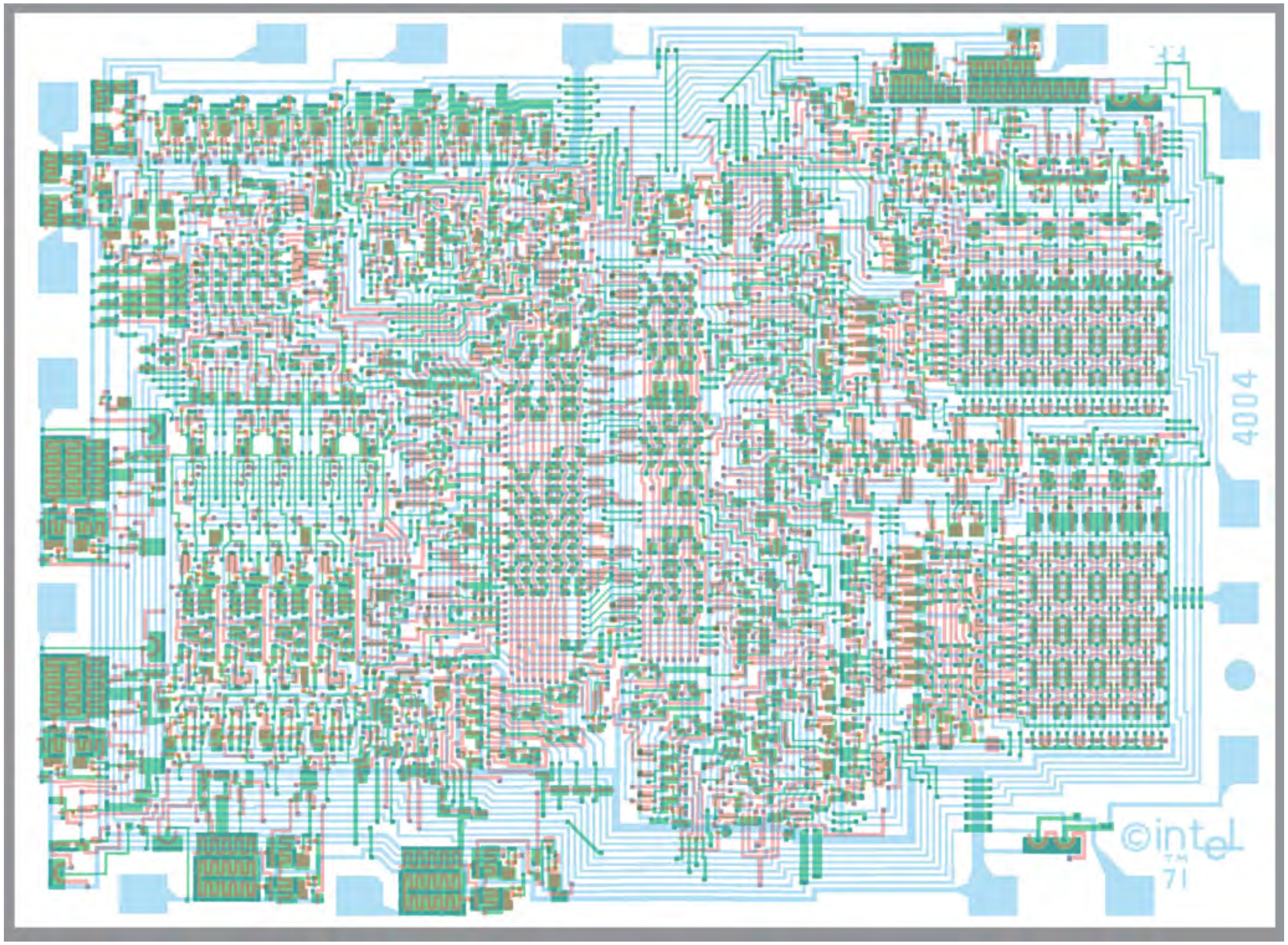




$$\text{reduced mass} \equiv \mu = \frac{m_A m_B}{m_A + m_B} \qquad \frac{\mu(I^{37}Cl)}{\mu(I^{35}Cl)} = 1.044 \qquad \frac{\mu(H^{37}Cl)}{\mu(H^{35}Cl)} = 1.0015$$

4.4% difference in vibrational levels

0.15% difference in vibrational levels

# Integrated Circuits on Si by Photolithography



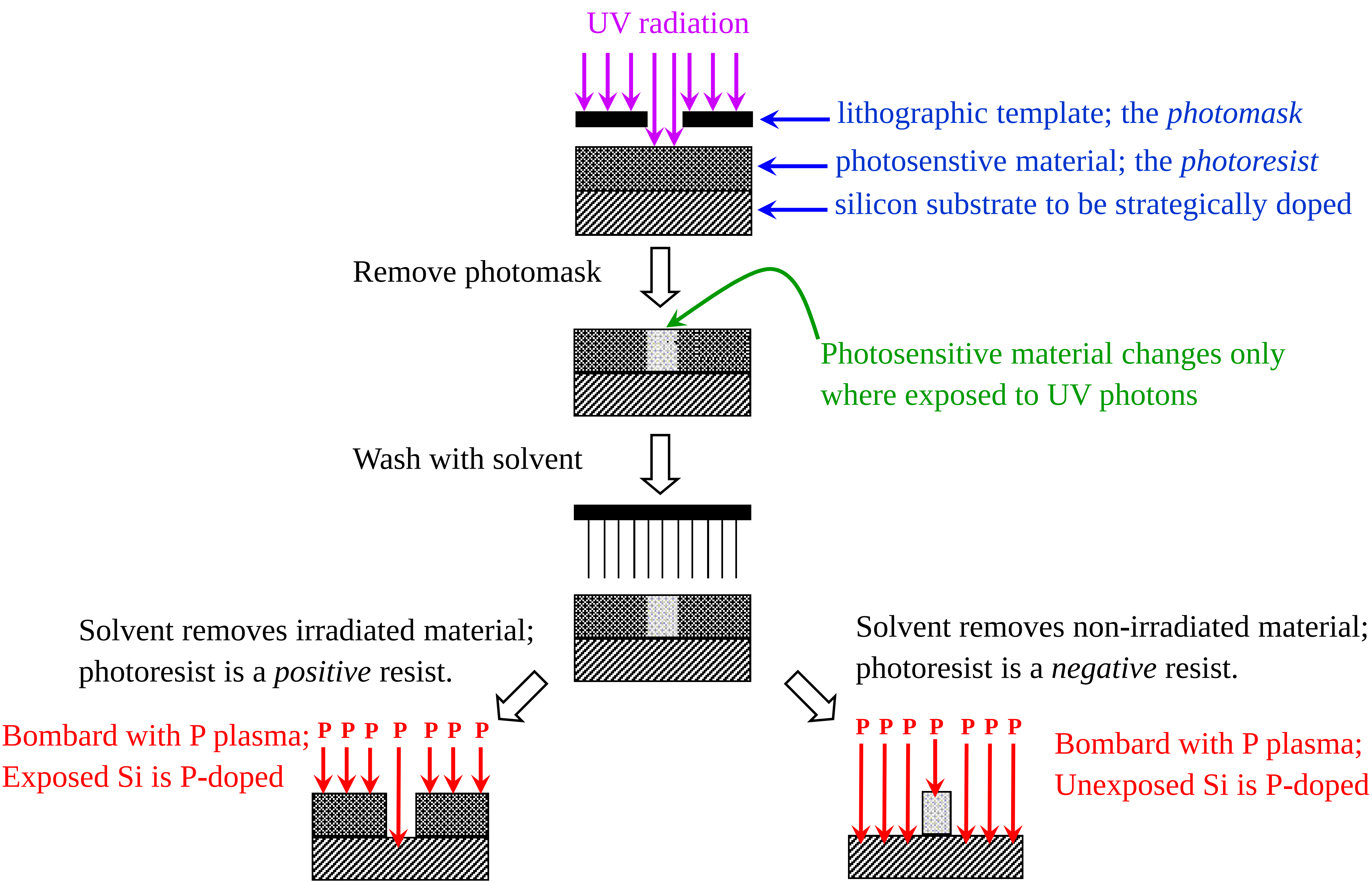

Intel’s 4004 Integrated Circuit - the first microprocessor (1971)

2300 solid state transistors!    Compare to 2300 electron tubes.

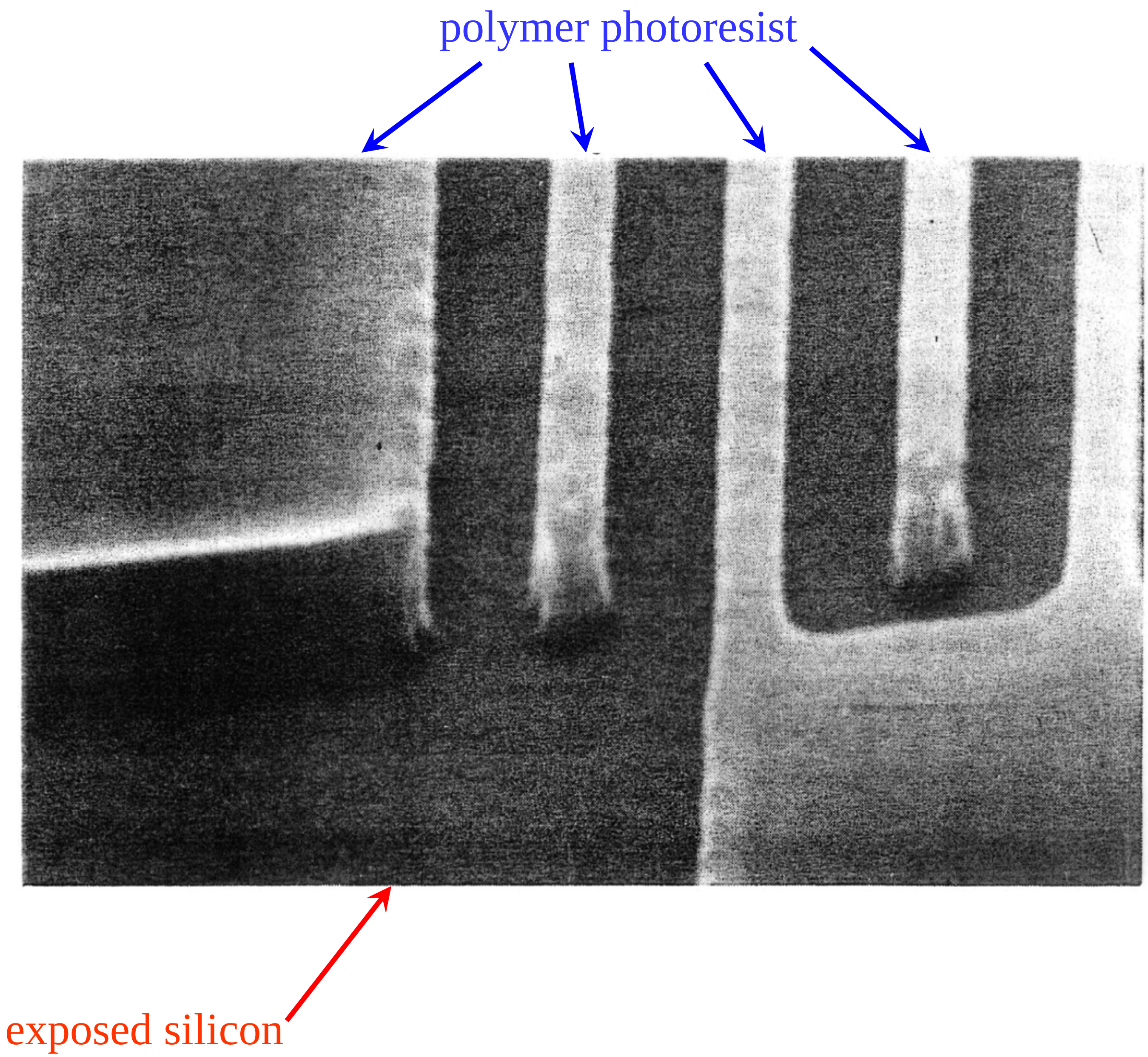
How to ‘draw’ conductive lines on silicon?

Recall:  Pure Si is a semiconductor.  P-doped Si is metallic.

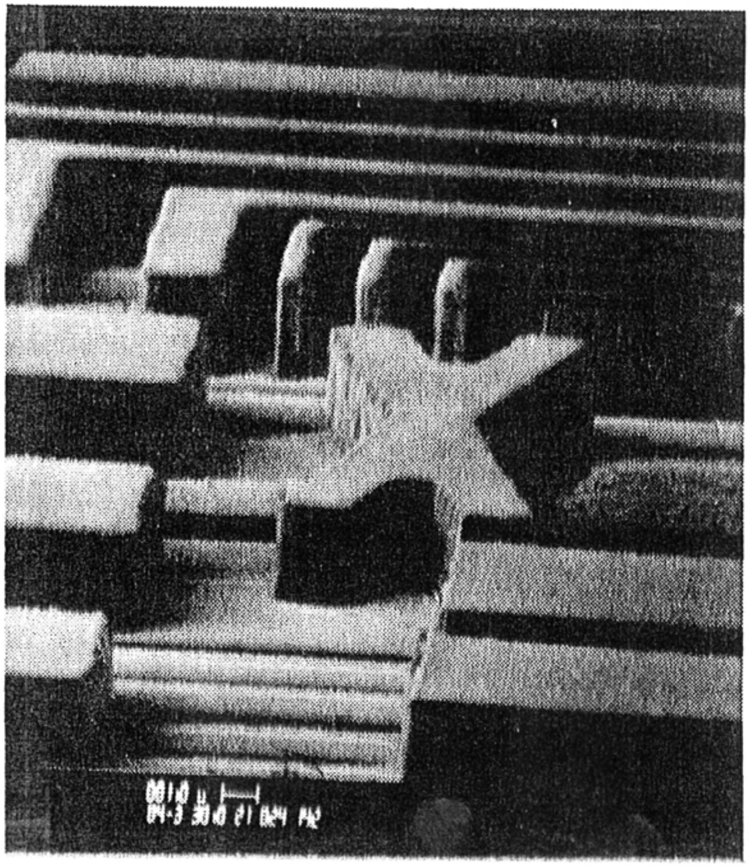
# Integrated Circuits on Si by Photolithography

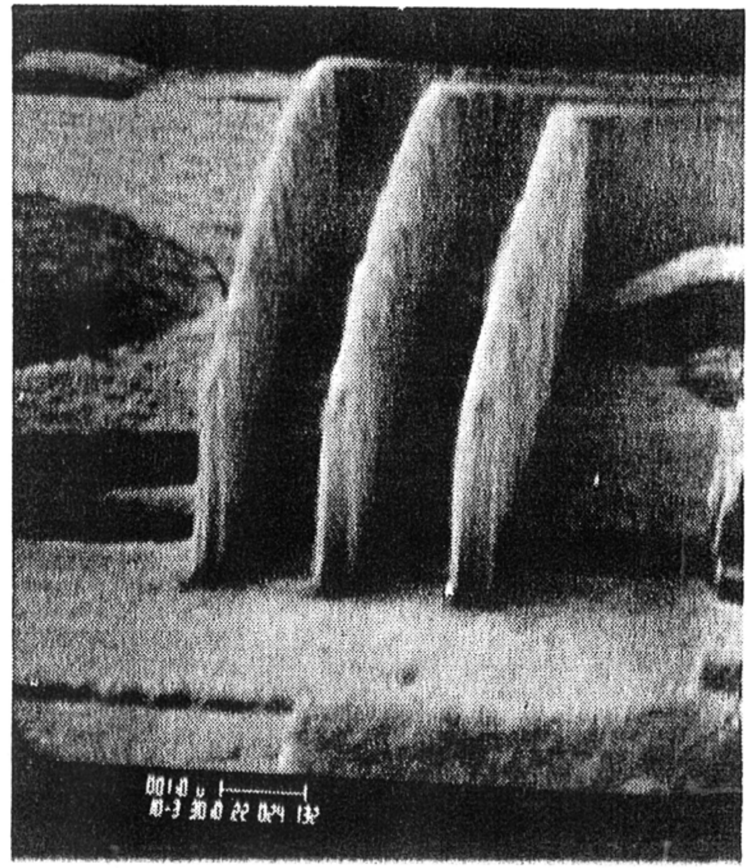


# Integrated Circuits on Si by Photolithography

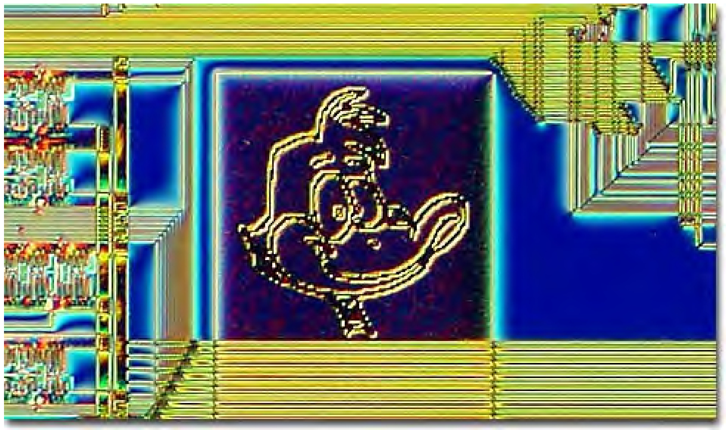


# Integrated Circuits on Si by Photolithography





# Integrated Circuits on Si by Photolithography

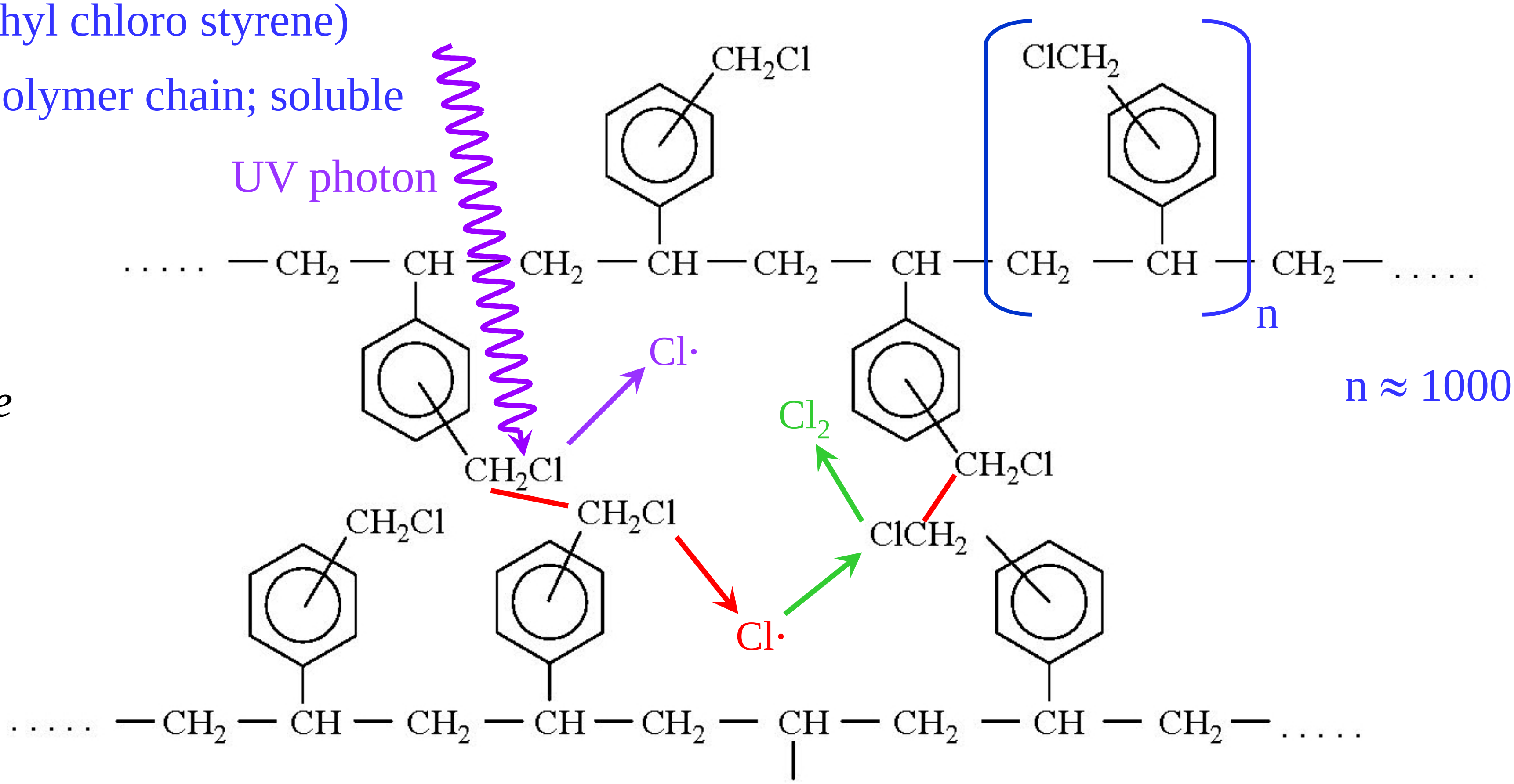


# Photolithography:  Mechanism of Elementary Reactions

Poly(methyl chloro styrene)

a linear polymer chain; soluble

*Before*




rxn 1. $-CH_2Cl + h\nu \rightarrow -CH_2\cdot + \cdot Cl$

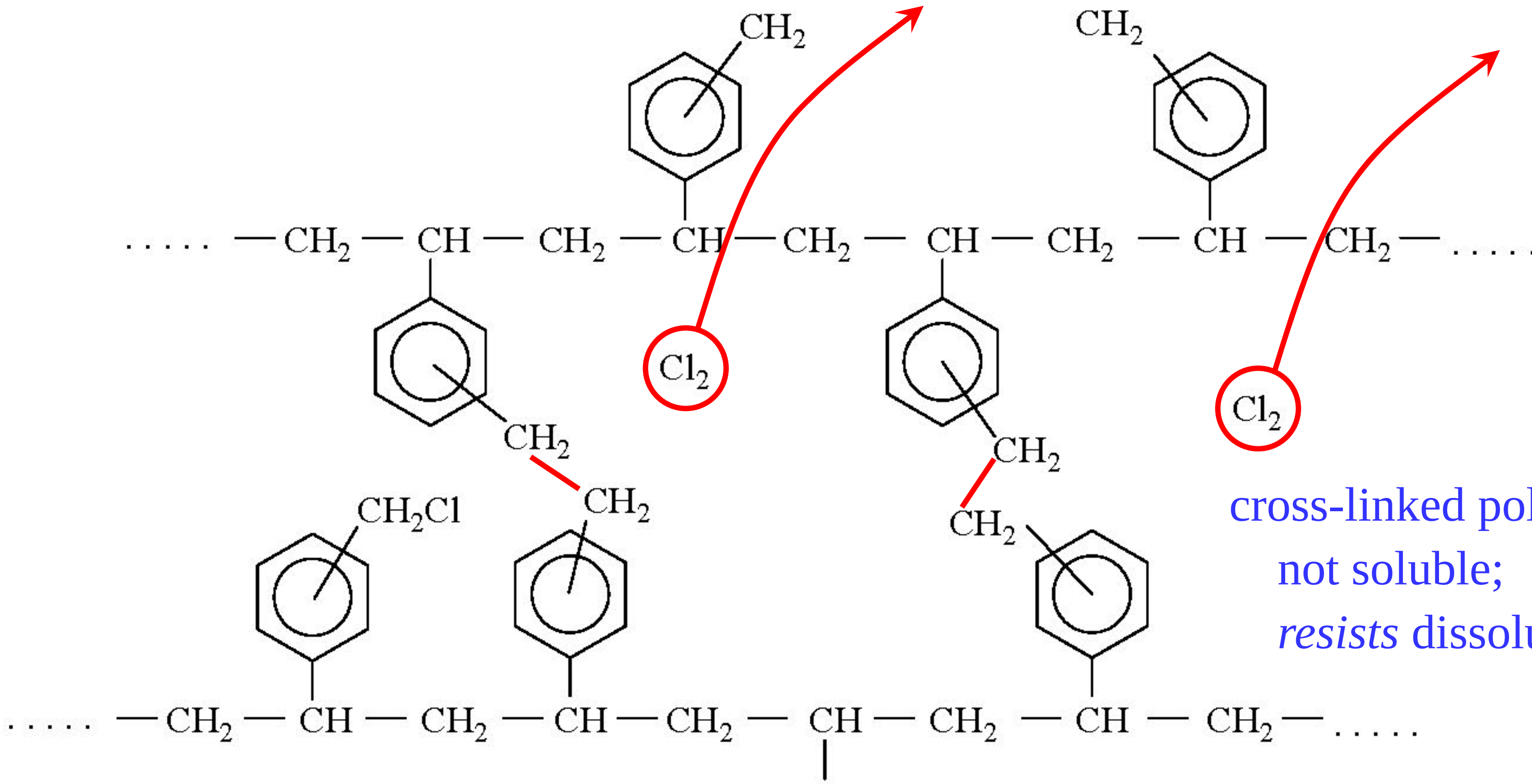
rxn 2. $-CH_2\cdot + -CH_2Cl \rightarrow -CH_2-CH_2- + \cdot Cl$

rxn 3. $\cdot Cl + -CH_2Cl \rightarrow -CH_2\cdot + Cl_2$

rxn 4. $\cdot Cl + \cdot Cl + M \rightarrow Cl_2 + M$

# Photolithography: Mechanism of Elementary Reactions

*After*




cross-linked polymer –
not soluble;
*resists* dissolution

forms negative pattern –
protects the Si surface
where irradiated

rxn 1. $-CH_2Cl + h\nu \rightarrow -CH_2\cdot + \cdot Cl$

rxn 2. $-CH_2\cdot + -CH_2Cl \rightarrow -CH_2-CH_2- + \cdot Cl$

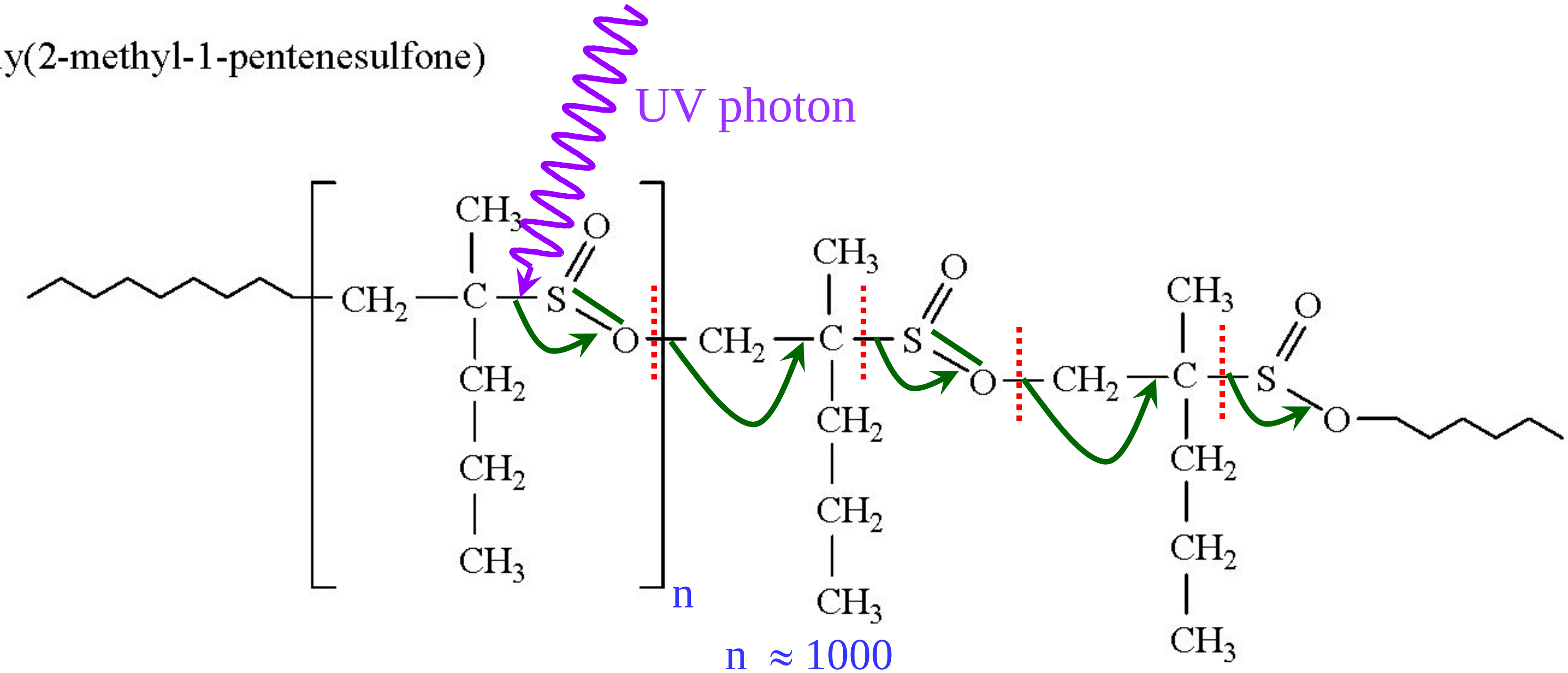
rxn 3. $\cdot Cl + -CH_2Cl \rightarrow -CH_2\cdot + Cl_2$

rxn 4. $\cdot Cl + \cdot Cl + M \rightarrow Cl_2 + M$

# Photolithography: Mechanism of Elementary Reactions

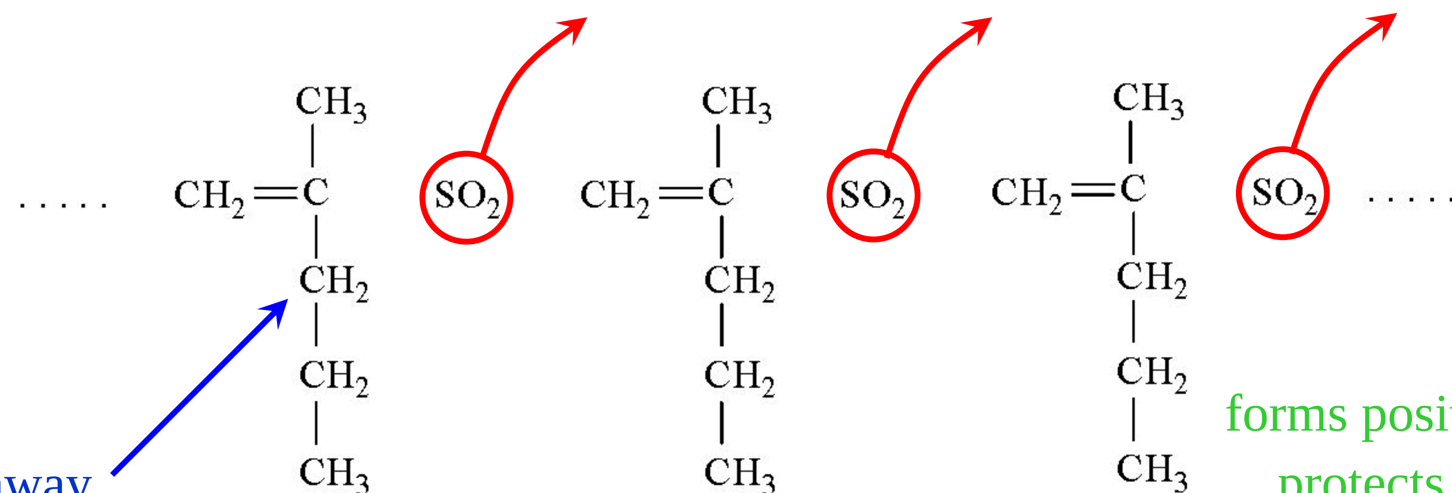
poly(2-methyl-1-pentenesulfone)

*Before*




One UV photon unzips the entire polymer chain. $\Phi = n\varphi = 10^3(0.1) = 100$

*After*




Wash away with solvent.

forms positive pattern – protects the Si surface where *not* irradiated