



***Photochemistry of common
spacecraft outgassing
contaminants: A review***

***Abraham N. Buditama
The Aerospace Corporation***

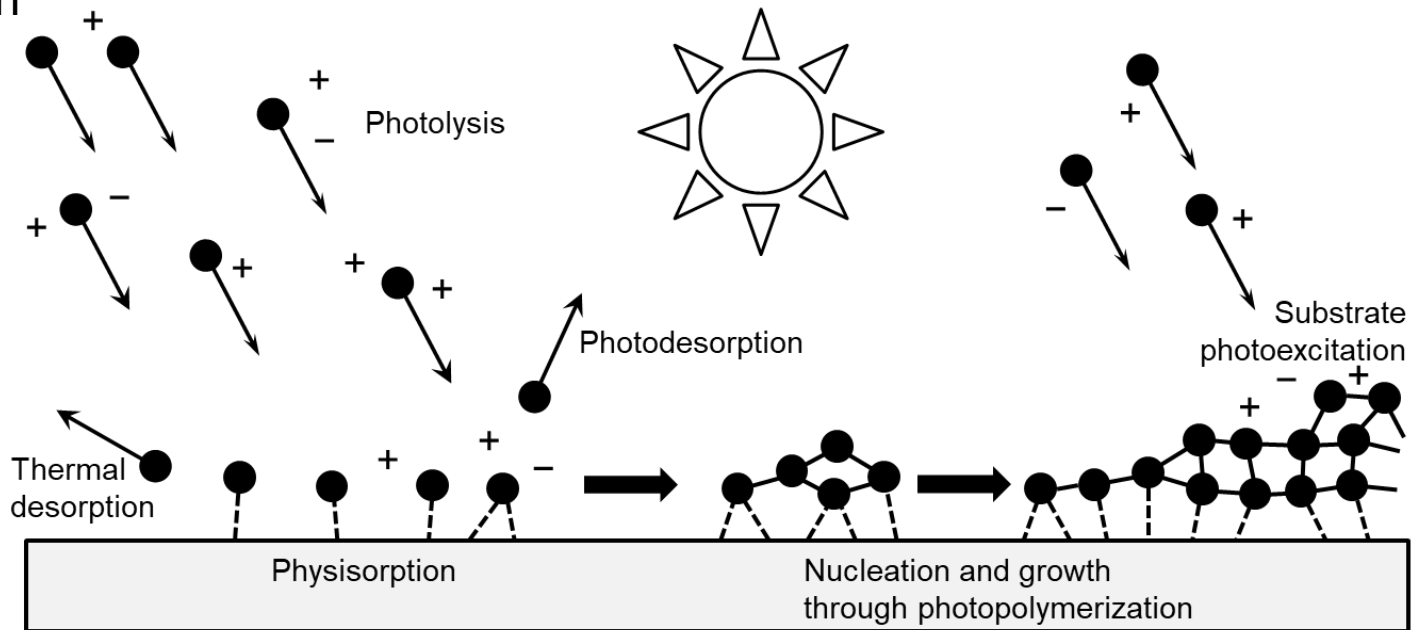
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Objective

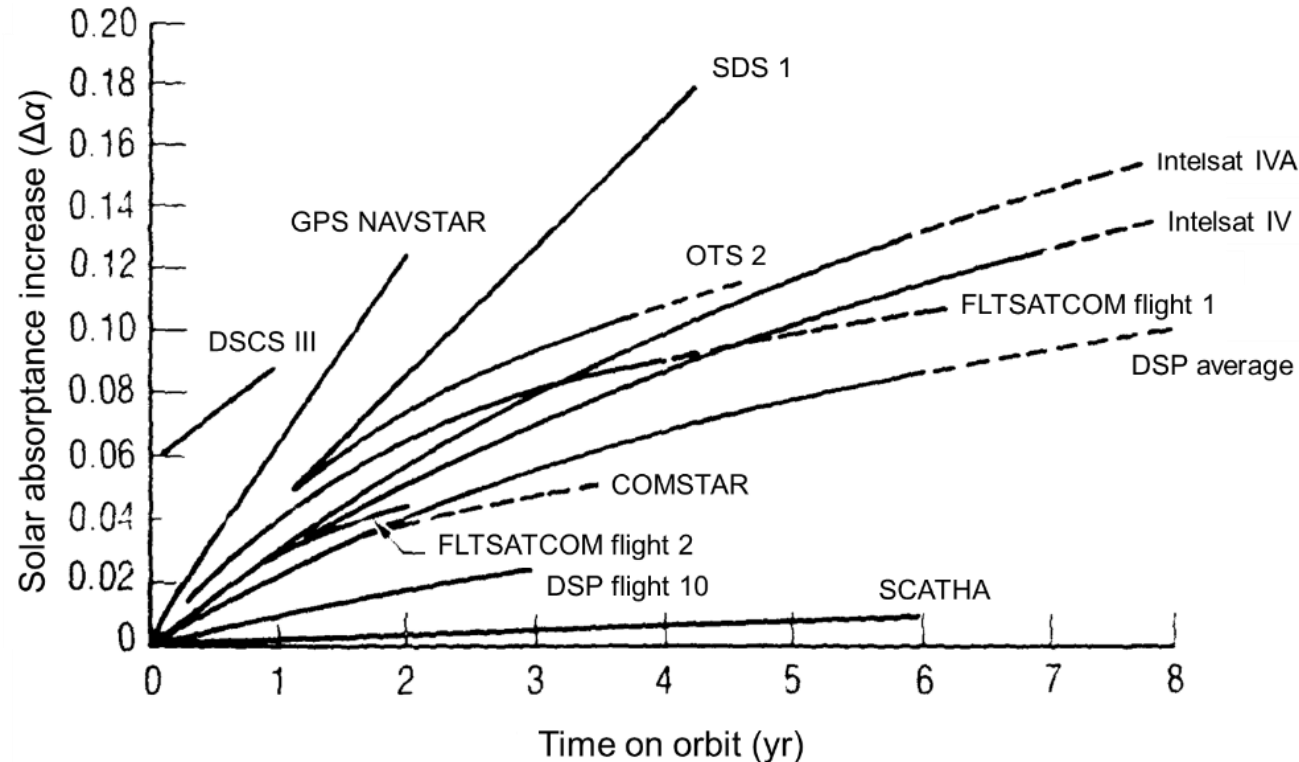


- To impress the importance of photo-induced molecular contamination
- To appreciate the complexities of VUV photochemistry
- To organize the knowledge gleaned from VUV research from the past three decades
- To highlight important parameters/components in VUV photodeposition research



The audience should walk away with a greater appreciation for VUV photochemistry

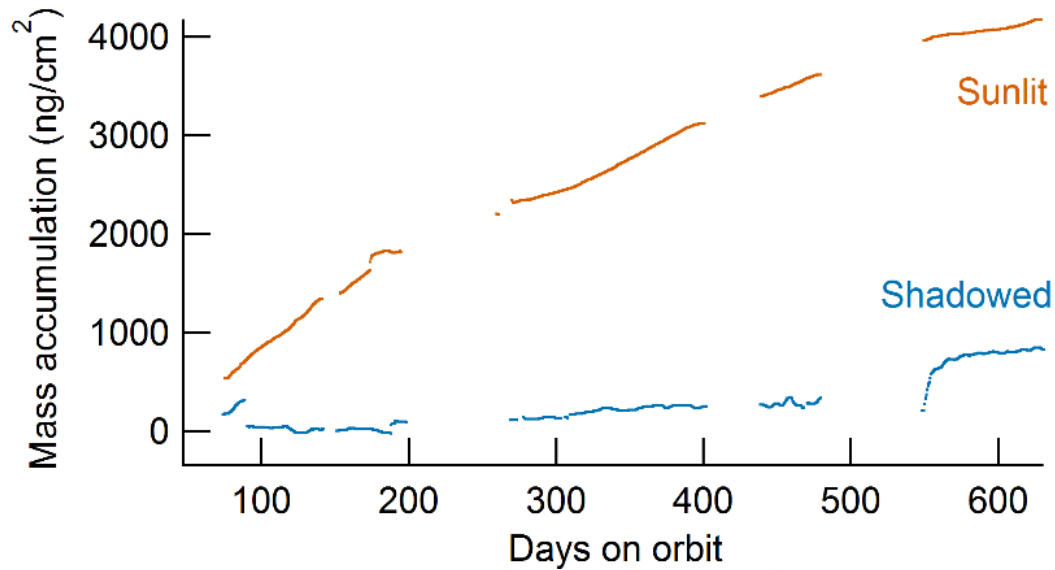
On-orbit degradation of thermal radiators



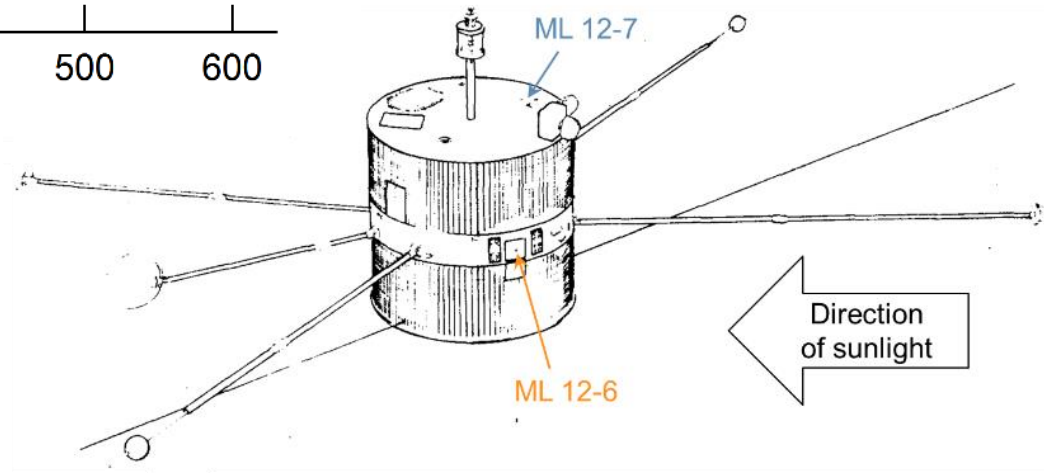
- Solar absorptance increase ($\Delta\alpha$) is a way to characterize contaminant degradation
- SCATHA spacecraft launched to quantify contaminant deposition in GEO
- SCATHA was engineered with good contamination control

Spacecraft contamination can severely hinder on-orbit performance

SCATHA sunlit vs. shadowed TQCMs



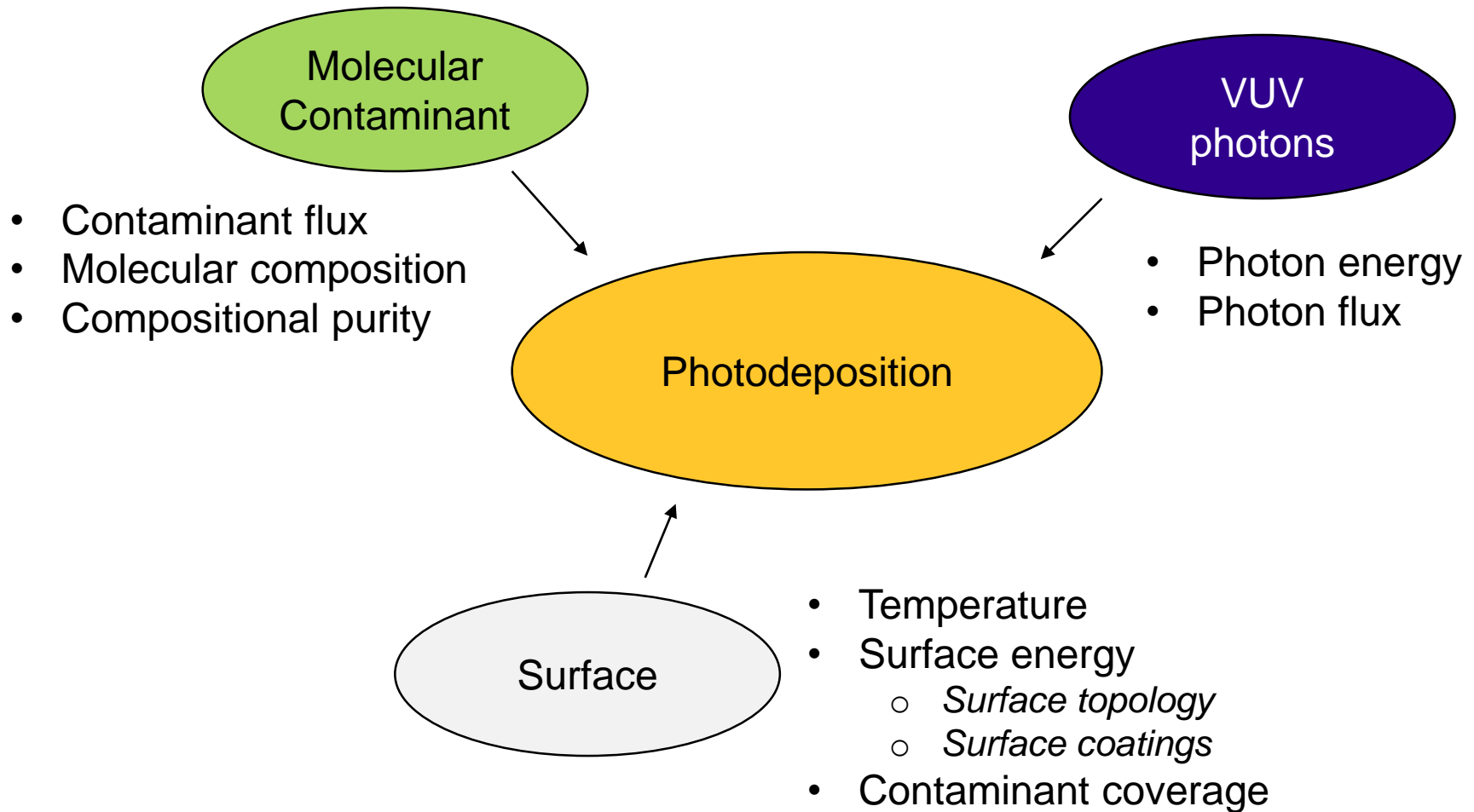
TQCM exposed to sunlight reports much higher contaminant accumulation



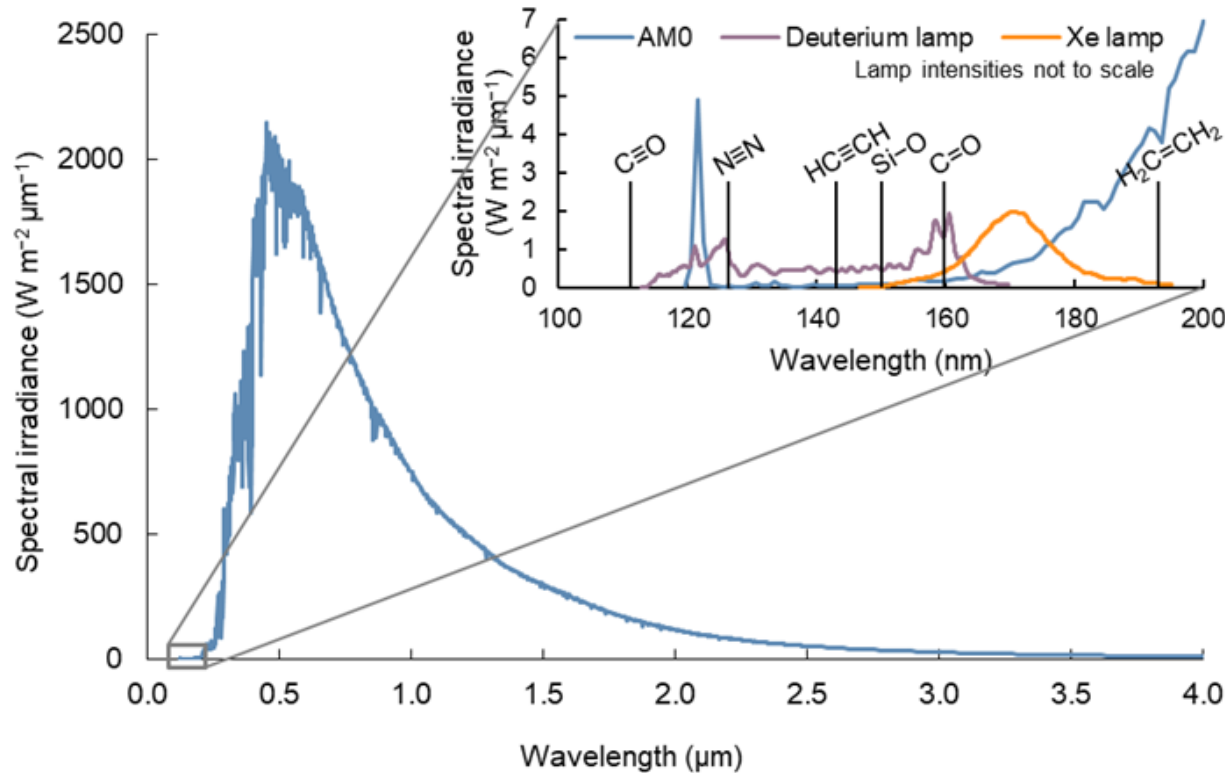
Typically, less contamination is expected on warmer surfaces

TQCM data shows evidence of VUV-induced contaminant accumulation

What governs photodeposition?



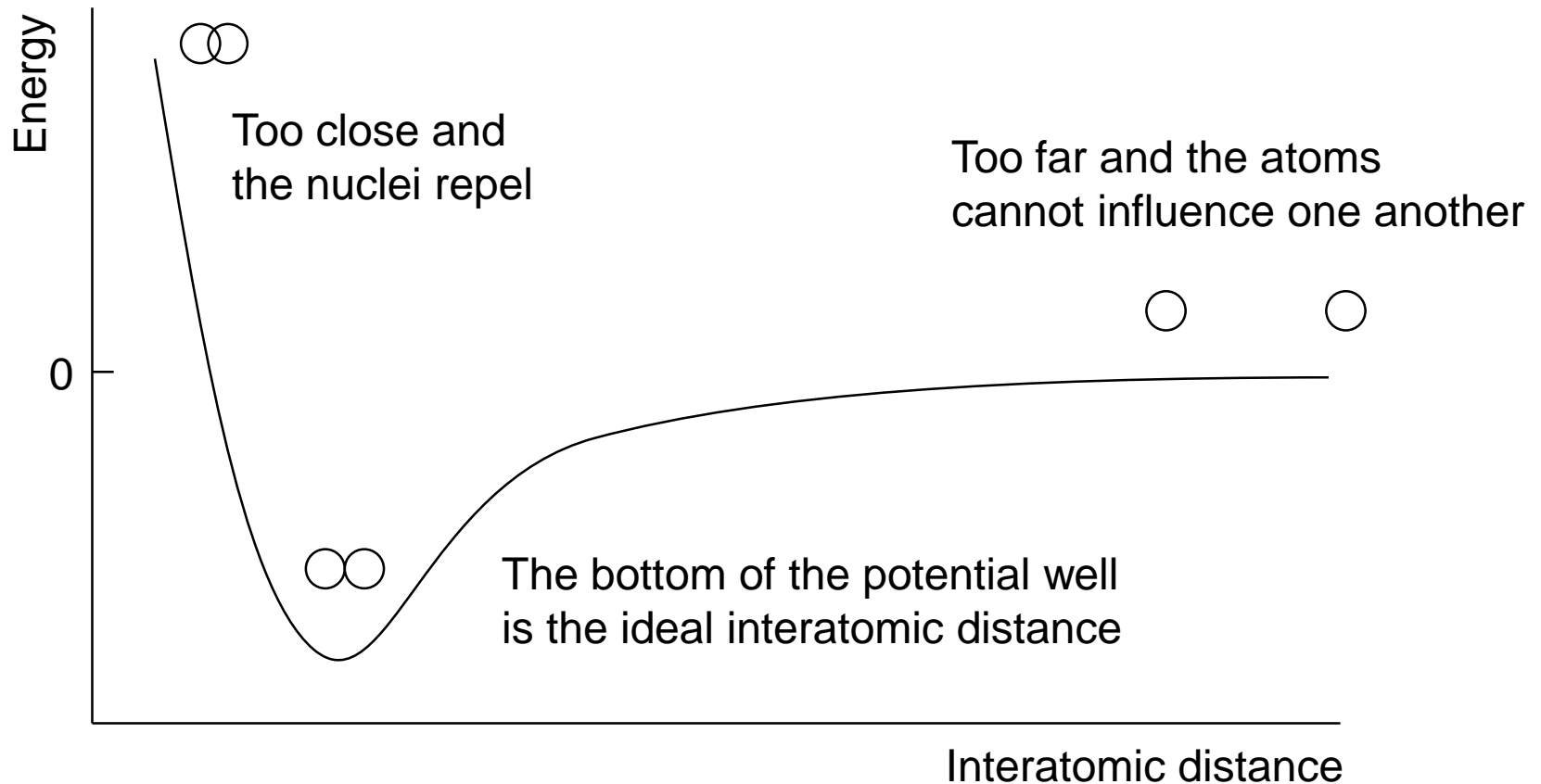
Vacuum ultraviolet (VUV) solar spectrum



- Atmospheric O_2 absorbs photons $< 200 \text{ nm}$
- Peak at 122 nm is hydrogen Ly- α line
- The bond dissociation energies shown here are for very strong bonds
- VUV can cleave through most chemical bonds

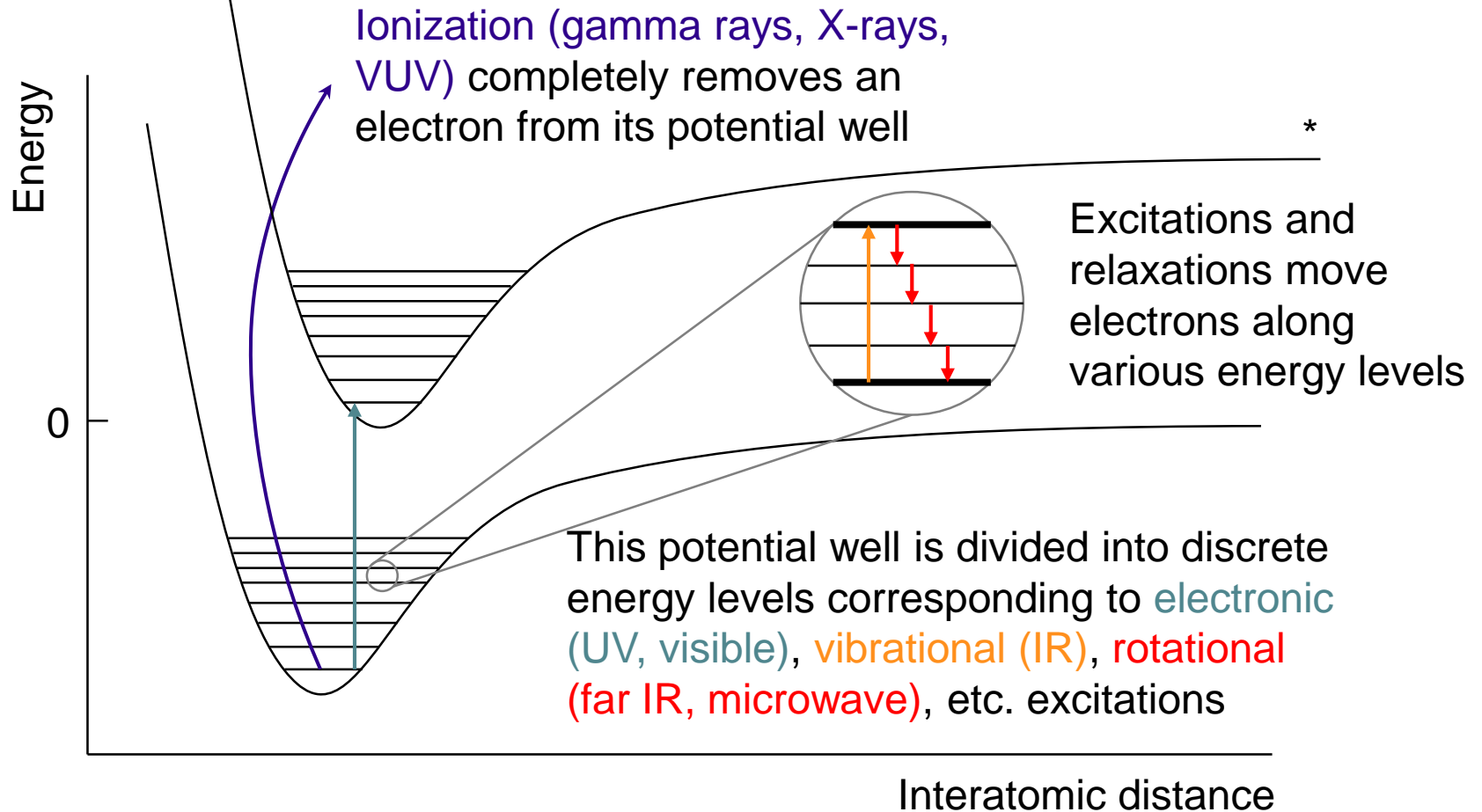
The VUV portion is small but has the highest energies

Review of chemical bonding



A chemical bond is a potential well, and electrons can be excited out of it by photons

Review of chemical bonding

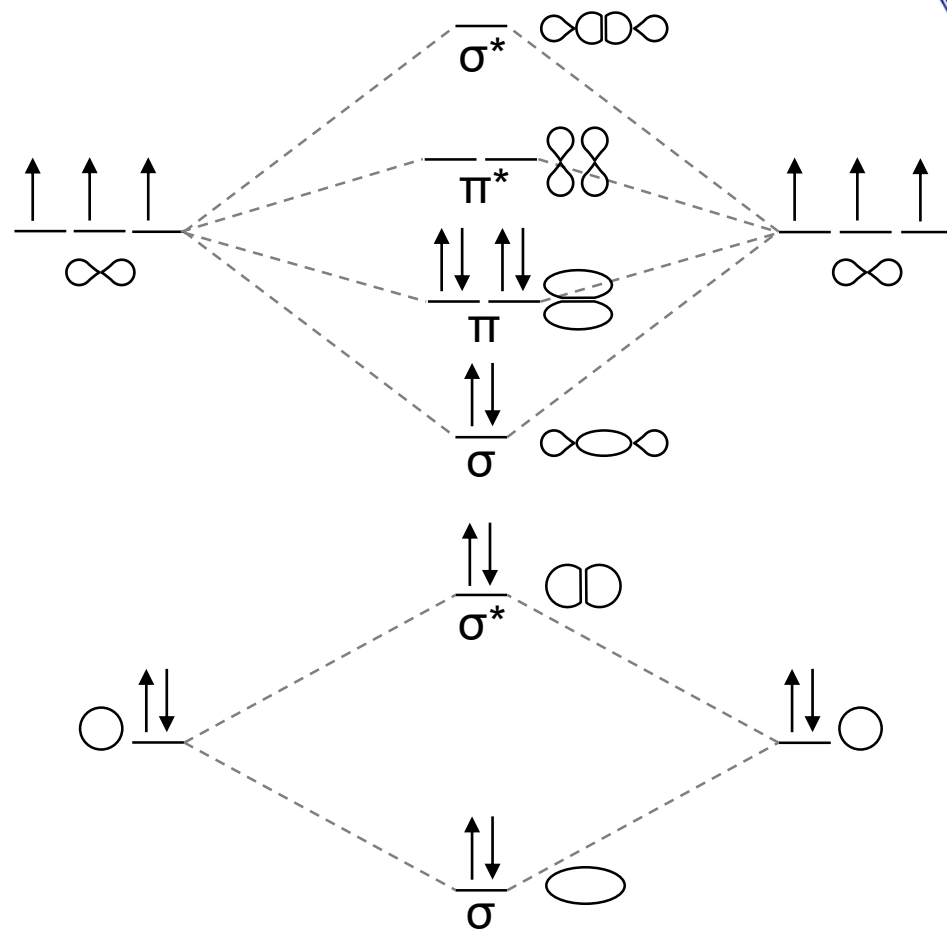


A chemical bond is a potential well, and electrons can be excited out of it by photons



Review of molecular orbital theory

- Atomic orbitals combine to make bonding and antibonding molecular orbitals
 - *In quantum terms, a linear combination of two atomic electronic wavefunctions output a lower-energy wavefunction with ℓ angular nodes and a higher-energy one with $\ell + 1$ angular nodes*
- The spacing between the energy levels determine what wavelengths can be absorbed
- Molecules with π bonds (things with multiple bonds, aromatic groups, etc.) tend to have smaller spacings between energy levels than those with σ bonds (things with single bonds)

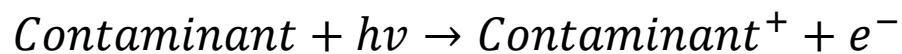


Excitation to an antibonding orbital is sufficient to make a chemical bond unfavorable

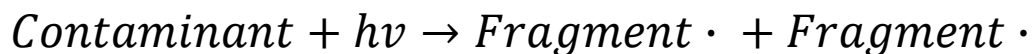


Possible photoexcitation pathways

Ionization



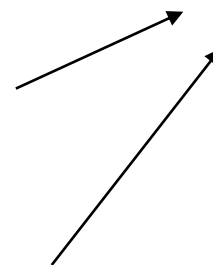
Radical formation



Transient excited state

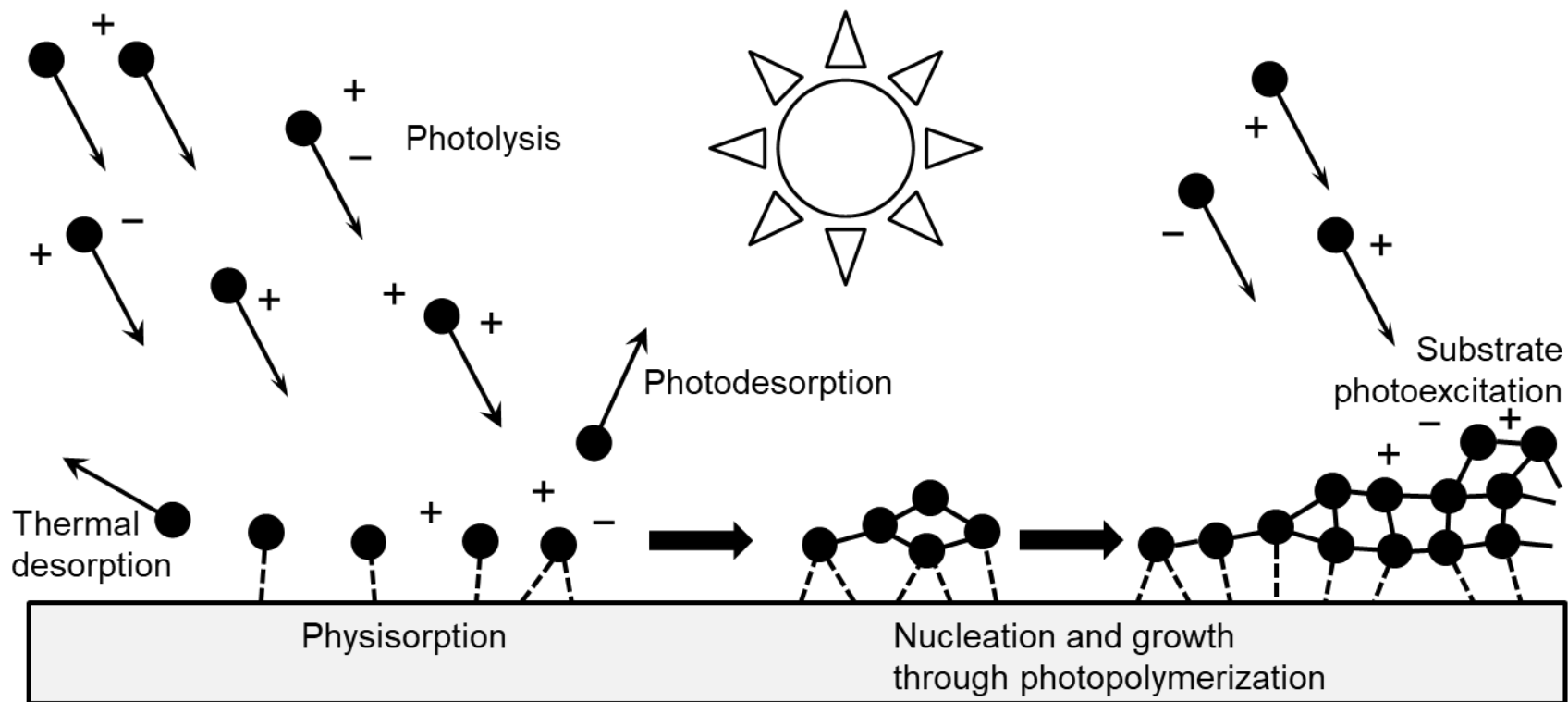


Bond cleavage



Photoexcitation can take many pathways and does not always lead to breaking bonds

VUV photochemistry reaction mechanisms

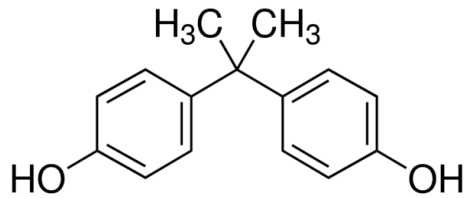


VUV induces many competing reactions

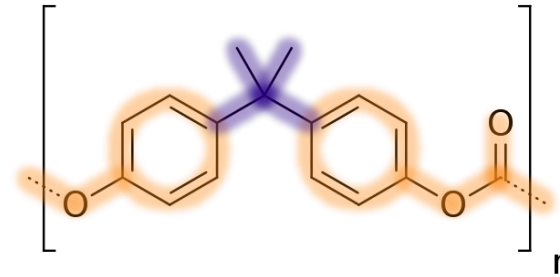


Bisphenol A polycarbonate photochemistry

Terrestrial empirical data

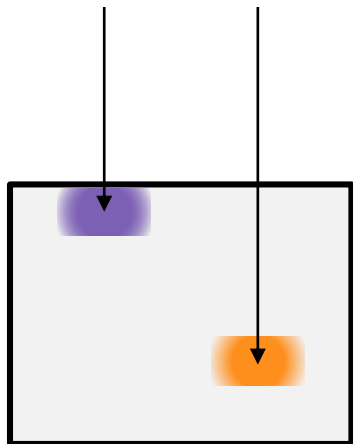


Polymerization →



Far UV tends to excite **these**
Mid UV tends to excite **these**

Far UV Mid UV



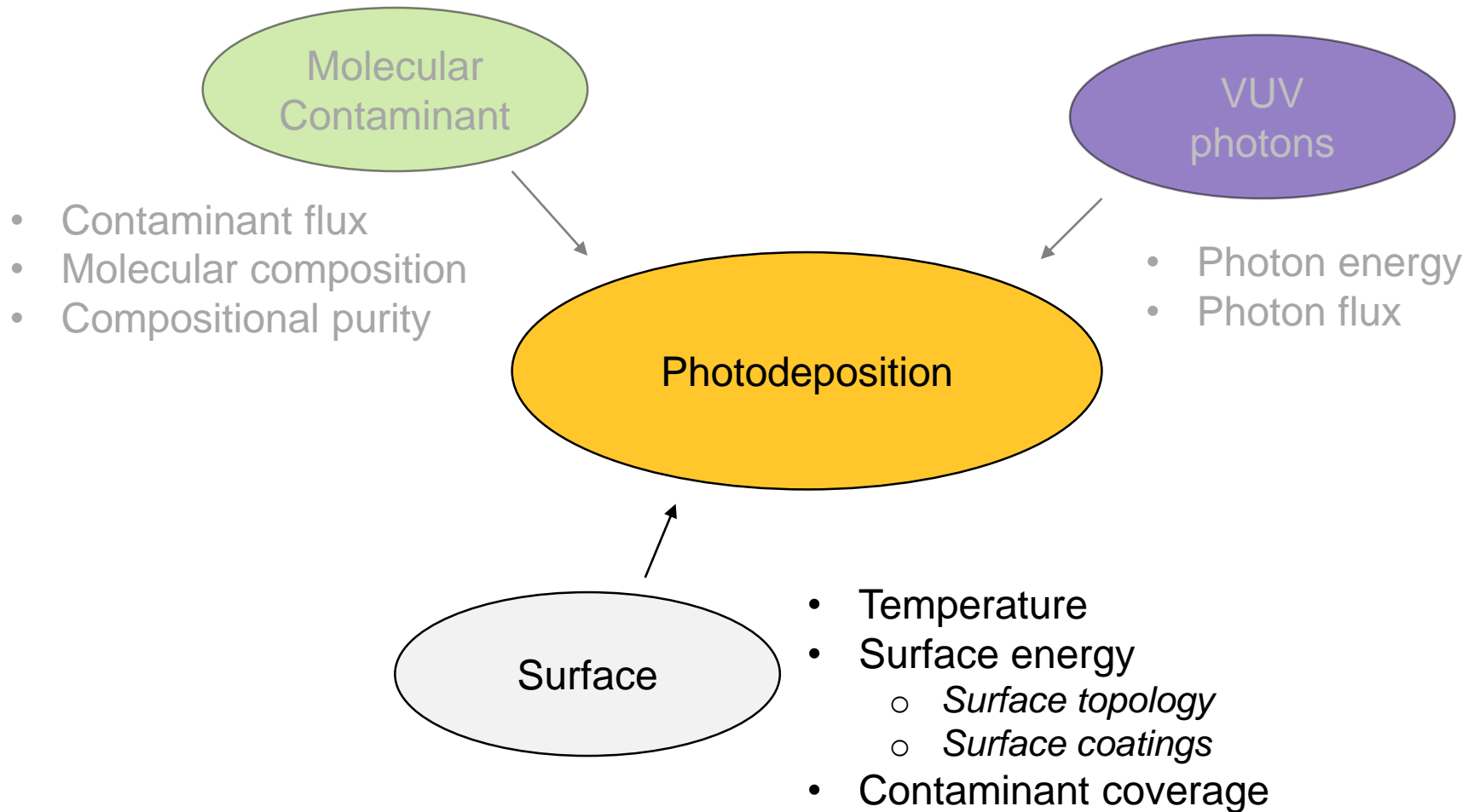
VUV is strongly absorbed and penetrates only a thin surface layer of solid PC

- Electrons in **π systems** (aromatic rings and conjugated bonds) are more delocalized, so excitations can dissipate more easily without bond cleavage
- Excitations in **σ bonds** (single bonds) are more likely to break them, causing small-molecule volatilization and cross-linking

[Adams 1993]

Chemical bonds of contaminants affect what kind of reactions can occur

What governs photodeposition?



Substrate effects

Temperature

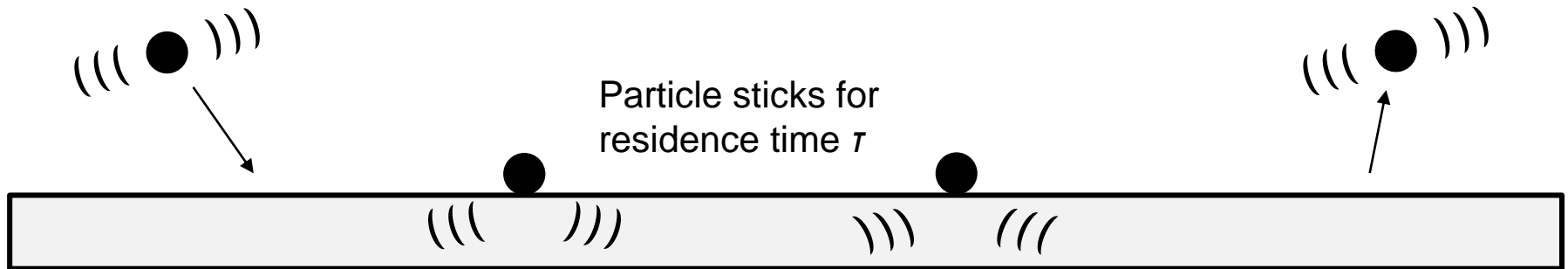


Without VUV

- A molecule gains enough energy to desorb from a substrate
- The colder it is, the less likely that desorption would occur
- Thus contaminants accumulate more on colder surfaces

With VUV

- Photofixing can occur in spite of warm temperatures (as on SCATHA) [Hall 1983]
- Overall desorption rate is a competition between thermal desorption, photodesorption, and photopolymerization [Olson 2008]
- Cold temperatures could inhibit photofixing [Nghiem 2009], but this does not inhibit physisorption to cold surfaces



Without VUV, desorption purely thermal; with VUV, photodesorption + photopolymerization

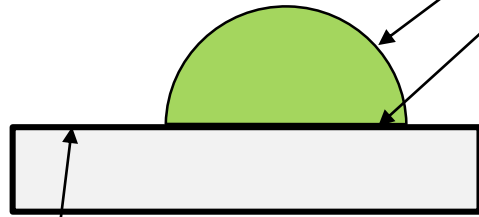
Substrate effects

Surface energy



Physics of wetting

If the solid–liquid interface + the liquid–vapor interface is low-energy, wetting is favored

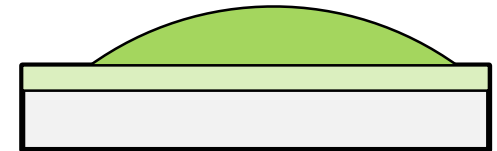
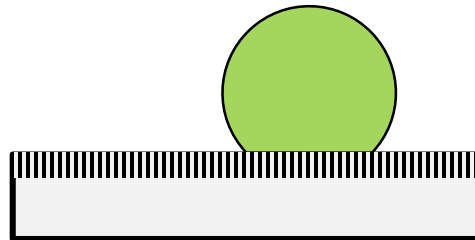


$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv})$$

[Coleman 2010]

If $S < 0$, droplets
If $S \geq 0$, films

If the solid–vapor interface is low-energy, wetting is not favored



Can control surface energy through topology or through material coatings

The morphology of contaminants can be controlled by substrate surface energy

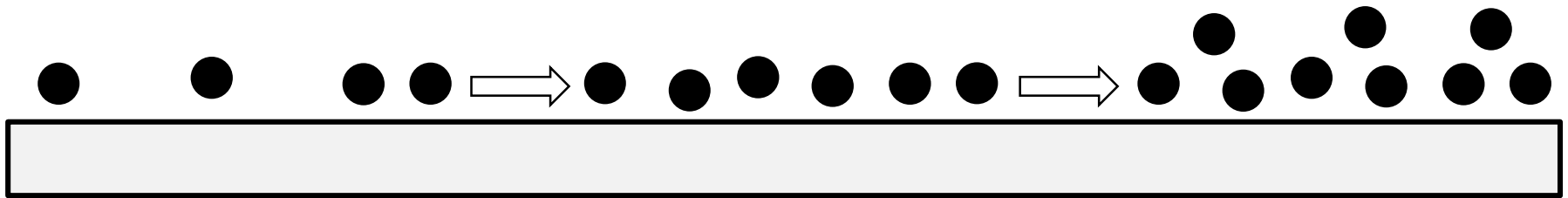
Substrate effects

Contaminant coverage

Photodeposition rates depend on physical adsorption rates

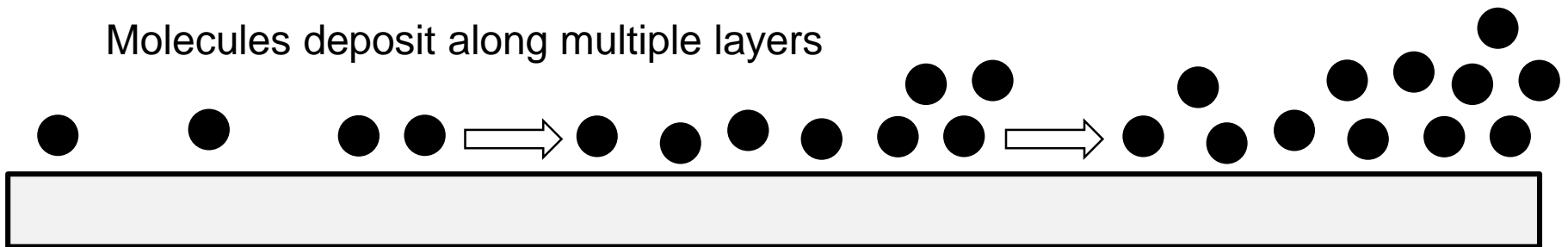


Molecules deposit monolayer by monolayer



Langmuir adsorption [Stewart 1989]

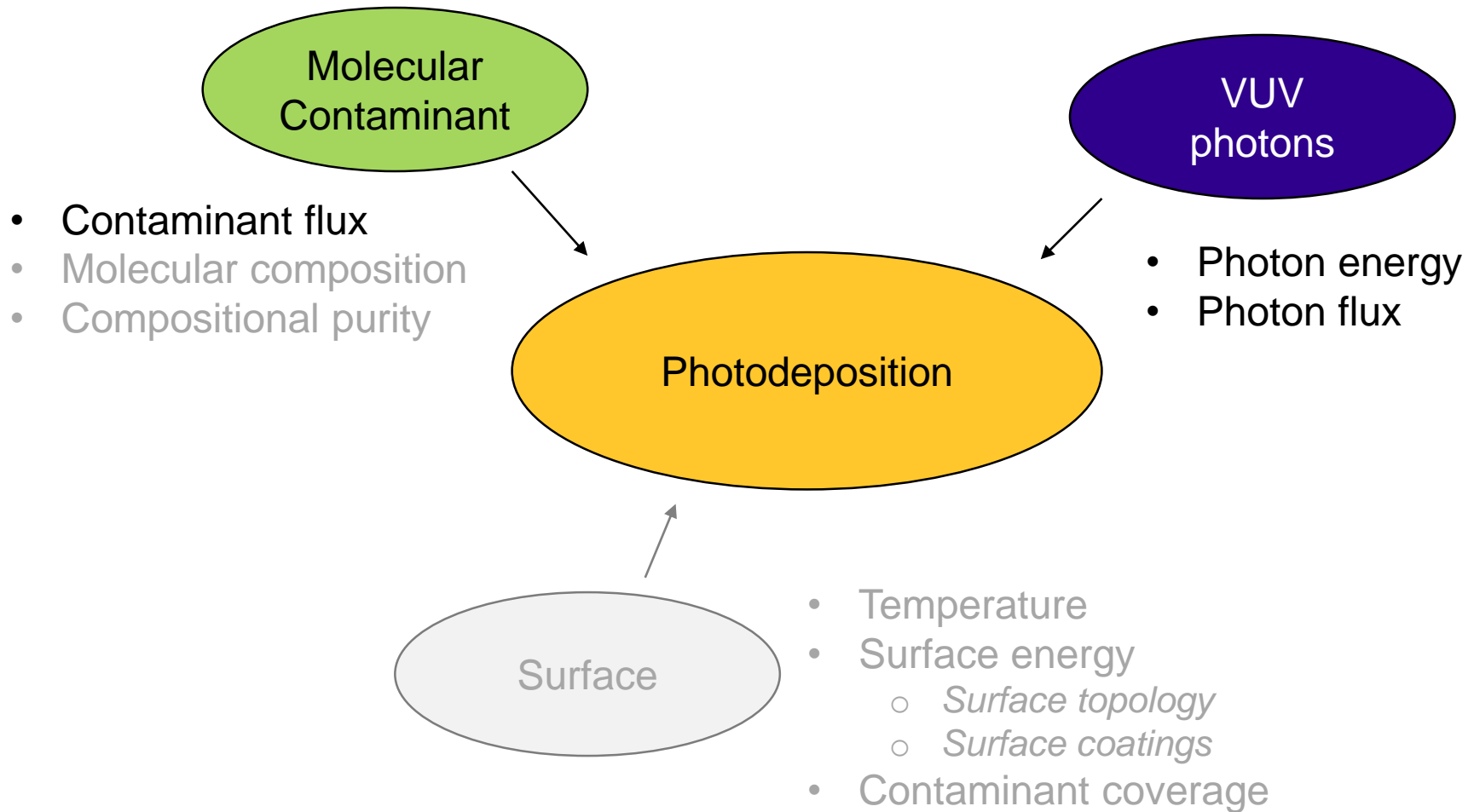
Molecules deposit along multiple layers



BET adsorption [Glassford 1992, Pereira 2006, Olson 2008]

Contaminant sorption differs between bare substrate and on adsorbed contaminants

What governs photodeposition?

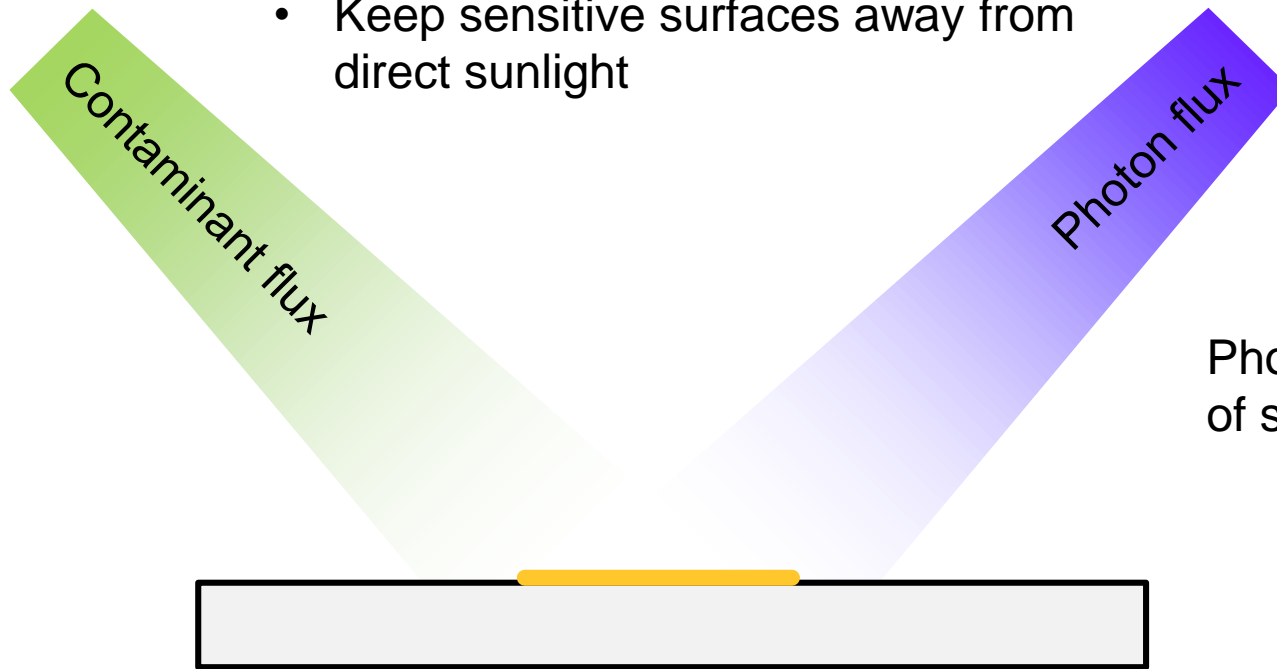


VUV and Contaminant Effects

Photon flux and contaminant flux

Either contaminant flux or photon flux could be rate-limiting, so minimizing them could reduce potential photodeposition:

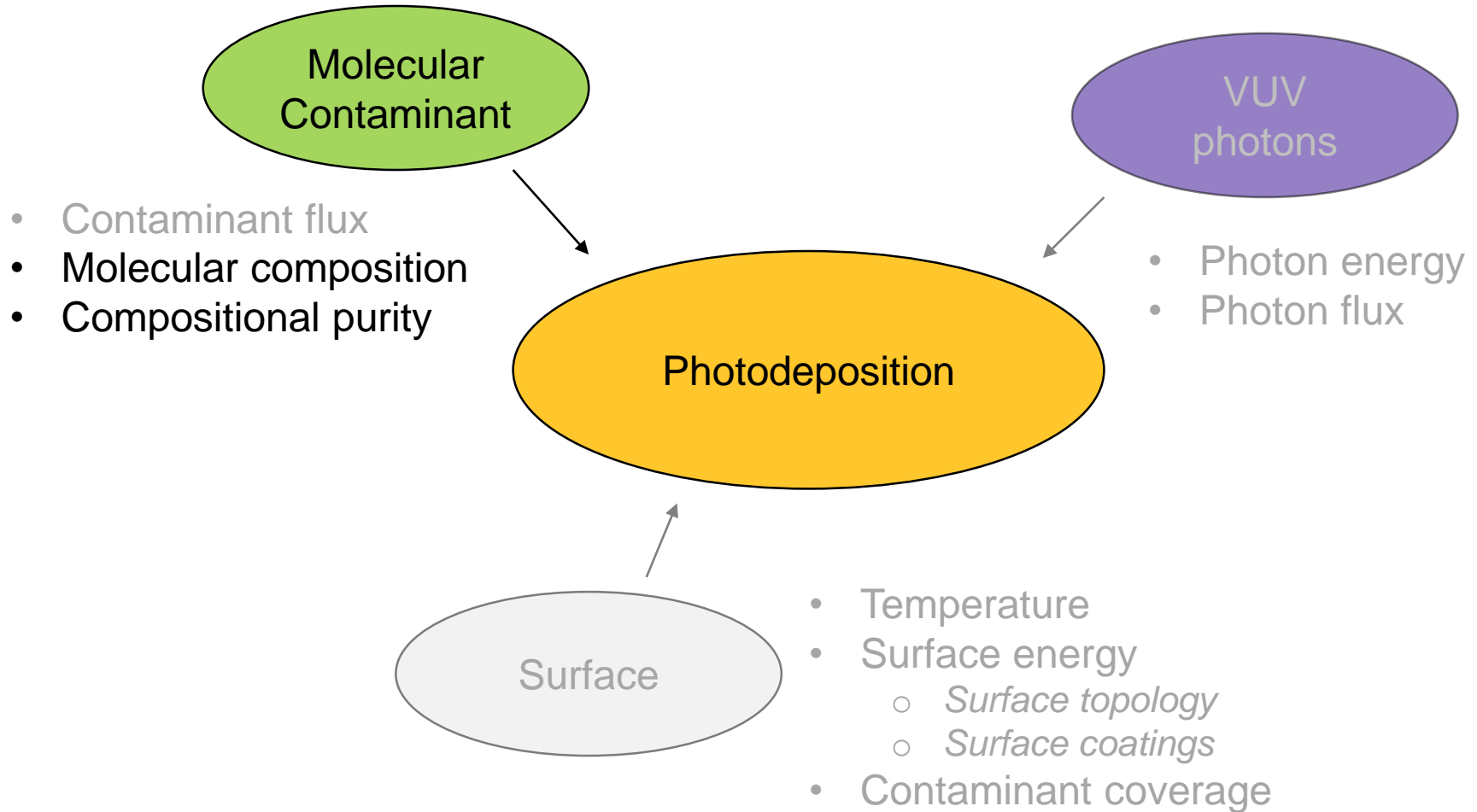
- Minimize view factor of contaminant sources
- Keep sensitive surfaces away from direct sunlight



Photons also need to be of sufficiently high energy

When system is photon-rich, contaminant is limiting deposition rates, and vice versa

What governs photodeposition?



Contaminant Effects

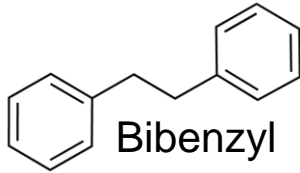
Molecular composition



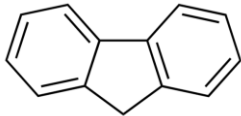
Known to NOT
photodeposit



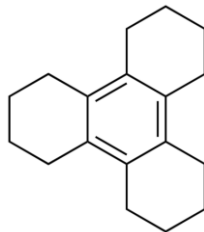
Benzene



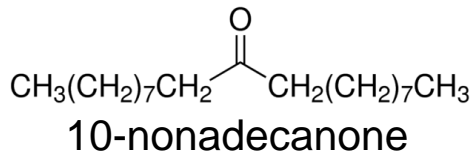
Bibenzyl



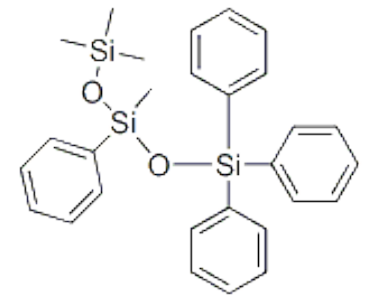
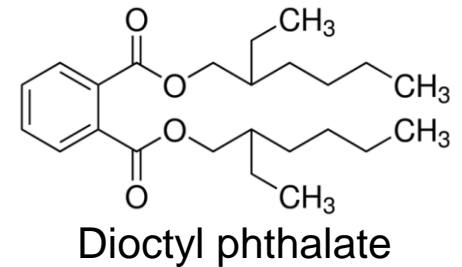
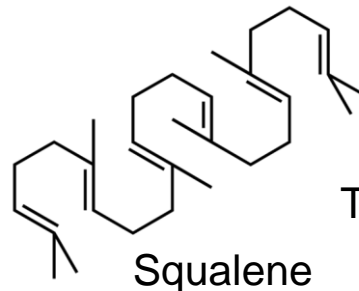
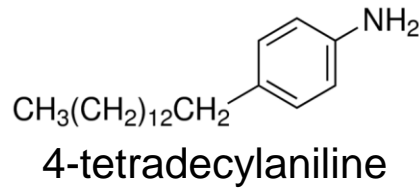
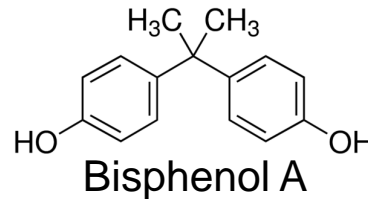
Fluorene



Dodecahydrotriphenylene



Known to
photodeposit

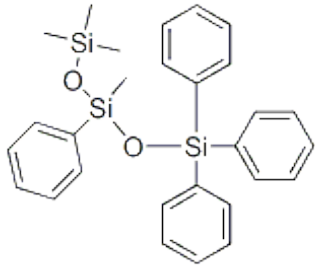


Certain classes of materials are more likely to photodeposit

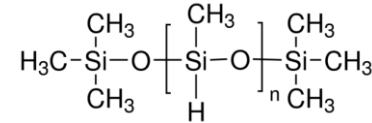


Contaminant Effects

Compositional purity



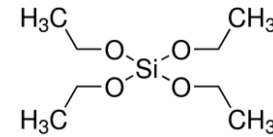
Silicones



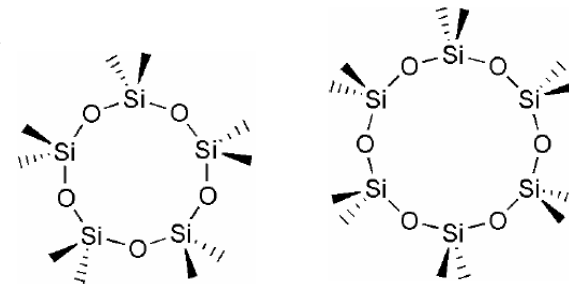
PDMS

SiO₂

Silica



TEOS



Cyclosiloxanes

[Villahermosa 2008, Hanrahan 2014]

- Outgassed species consist of many low-mass impurities
- Different photodeposition rates for multi-component systems [Luey 2008]
- Real spacecraft contaminants tend to be all mixtures

The nominal composition of a material can be different from outgassed species

Summary of contaminant literature



Year	Authors	Contaminants	Substrate	UV source	Major findings
1983	Hall ²	flight contaminants from SCATHA mission	QCM	Sun	SCATHA TQCM data show evidence of VUV-induced contaminant accumulation
1985	Hall, et al. ⁴				
1988	Arnold, Hall ³				
1988	Stewart, et al. ⁵	DC-704, DEHP	QCM, Au, Al, MgF ₂	Kr/Xe lamps	Laboratory results confirm VUV-induced irreversible deposition; deposition rate inversely dependent on temperature upon irradiation
1989	Stewart, et al. ⁶				A Langmuir-like model (ideal contaminant vapor, substrate perfectly flat, adsorbed molecules do not interact) of photochemical deposition proposed, and empirical fitting was done to infer the kinetic parameters
1992	Frink, et al. ⁷	DC-704 equivalent	QCM, MgF ₂	Xe lamp	Measured outgassing rates and optical transmission; solvent/wiping partially removed photodeposited film
1993	Adams, Garton ²⁰	BPA PC	—	Deuterium lamp	Spectroscopic determination of solid BPA PC VUV photochemical mechanisms; VUV absorbed mostly in a thin surface layer
1996	Arnold, Luey ¹⁵	DEHP, BPA, DC-704, others	QCM, fused silica	Kr/Xe lamps	Explored which classes of molecules photodeposit (phthalates, phenols, aromatic amines, silicones, alkenes) and which do not (aromatic hydrocarbons, aliphatic carbonyls)
1996	Shaw ³⁸	DC-704	QCM	Ly- α lamp, Hg lamp	Showed different rate regimes for sub-monolayer coverage; deposition rates from a Ly- α photon about 6 times higher than from a 180 nm photon
1996	Tveekrem, et al. ²⁹	Real on-orbit contaminants	MgF ₂ - and Al-coated mirrors	Earth albedo	Onboard contamination from Hubble presents as non-uniform haze with droplet morphology; gentle cleaning with detergent and acetone recovered optical lens transmission, confirming that degradation is attributed to contamination only
1998	Arnold ¹⁶	—	—	—	Proposed deposition and desorption kinetics for different monolayer coverages, Clausius–Clapeyron or Raoult behavior for pure substances and mixtures respectively, and outgassing rates for diffusion-controlled desorption
1998	Fong ⁵³	—	—	—	Proposed time-dependent sticking coefficient theory for photoexcited vs. ground state contaminants ; sticking coefficient should decrease with time; photoexcitation rate must exceed thermal desorption rate for photodeposition to occur
2003	Pereira, et al. ⁸	DEHP	QCM	D lamp	Expanded Stewart et al.'s model of photodeposition kinetics; included temperature, surface coverage, and desorption effects; compared with experimental results
2006	Albyn, Burns ¹⁷	Epoxies, rubbers, adhesives, oils	QCM	D lamp	Observed contaminant photodesorption by VUV irradiation
2008	Olson, et al. ¹⁸	DEHP	QCM	D lamp	Photodesorption is reduced by low substrate temperatures; low VUV intensity led to VUV-induced desorption; high VUV intensity led to photopolymerization
2008	Luey, Coleman ³⁰	DEHP, DC-704	Si wafer	D lamp	VUV pre-irradiation of surfaces promotes droplets into contaminant films; photopolymerization rates slower for multi-component systems
2008	Ianno, Thompson ³⁹	RTV CV-2568	MgF ₂ -coated coverglass	Xe lamp, solar simulator	Postulated that the photodeposition process can be influenced by the relative abundance of contaminant molecules and photons (photon flux–limited regime vs. a contaminant flux–limited regime) via QCM and in situ ellipsometry
2009	Tondu, et al. ⁴⁵	BPA	QCM	D lamp	Pure contaminants can still give multiple TGA peaks because heating can induce contaminant phase changes; irradiation can lead to cluster morphology
2009	Nghiem, et al. ^{32,33}	Tridecan-2-one	QCM	D lamp	Observed that UV fluence has non-monotonic effect on less volatile products; low temperatures can inhibit photolysis and limit non-volatile residue
2010	Coleman, Luey ³⁴	Epoxies, silicones, phthalates	Si wafer, QCM	D lamp	VUV pre-irradiation of surfaces promotes films instead of droplets; increasing substrate surface energy suggested to be underlying reason
2012	Coleman, Luey ³⁵	DC-704, DEHP	Si wafer, QCM	D lamp	Various surface cleaning methods (piranha wash, deuterium lamp irradiation) suggest that stripping native SiO _x and adventitious carbon promotes film morphology as opposed to droplets; VUV photochemistry effective at removing this outer layer of adventitious carbon
2014	Hanrahan, Ianno ⁴¹	Silicones	Si wafer	Xe lamp	FTIR data shows that nominal composition of bulk materials differs from actual composition of outgassed species
2016	Roussel, et al. ¹⁴	BPA	QCM	D lamp	Numerical modeling of kinetics accounts for competition between fixation and desorption; photodeposition can occur even without concurrent VUV irradiation
2018	Luey, et al. ³⁷	Epoxies, silicones	Si wafer, Au, ZrO ₂ , HMDS	D lamp	Material coatings made to alter substrate surface energies are effective in changing contaminant morphology

Full table in manuscript

Conclusions



- Three primary components of VUV photodeposition

- *Substrate*

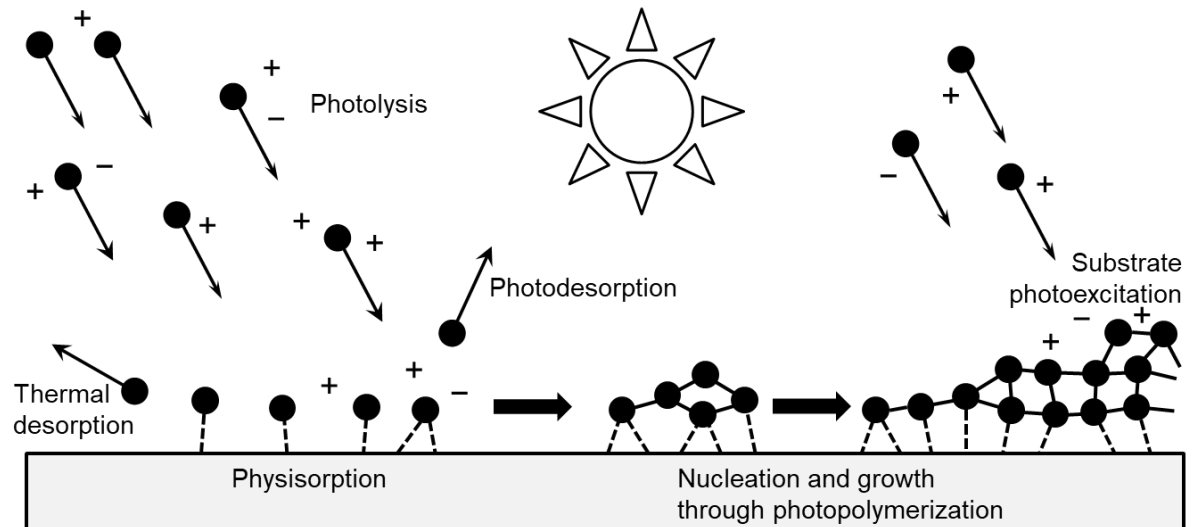
- Temperature
- Surface energy
- Contaminant overage

- *VUV*

- Photon energy
- Photon flux

- *Contaminant*

- Contaminant flux
- Molecular composition
- Compositional purity



- Overall deposition is a result of a competition between various photochemistry mechanisms, which can be pushed one way or the other by these different parameters