Outlook For Resist Design at 157 nm

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Outline

- Overview: Why 157 nm?
- Challenges for 157-nm resists
  - Difficulties in using existing resists
  - VUV absorbance of common polymers
  - Requirements for new materials
- Summary

Interest in Developing 157-nm Lithography is Growing

- Sematech's "Next Generation Lithography" (NGL) Conference on Dec. 10, 1998 revealed that many semiconductor companies are concerned about the timing of the NGL choices (EUV, EPL, IPL, X-Ray)

- 157-nm lithography emerged as an interim choice necessary to bridge the gap to the NGLs

- Recent advances in lasers and optical materials has encouraged the industry that 157-nm is technically feasible (although cost-of-ownership still remains a concern)

The 157-nm Challenge

- Potential technical “show stoppers” are materials related:
  - Pellicle materials (inorganic membranes, fluoropolymers)
  - Mask materials (fluorine-doped synthetic silica)
  - Resist materials (hydrofluoropolymers, siloxanes, etc.)
- Resist challenges are multifaceted
  - Transparency (use of thin layers)
  - Photochemistry (both desired and undesired)
  - Solubility and adhesion
  - Outgassing and contamination

The 157-nm Resist Challenges

- Using existing resists requires ultrathin resists
  - Defect levels in sub-100-nm resist layers may be an issue
  - Problem is similar to that faced by EUV resist efforts
- VUV photochemistry of existing resists not well studied
  - High G_x values can lead to reduced contrast
  - High G_s values can cause outgassing
- New routes: Little data exists for functional-group contributions
  - Absorbance must be weighed against other properties
    Solubility/etch resistance/transparency a three-way balance
  - Preliminary absorbance studies suggest possible routes

Ideal Scenario Would Allow Use of Existing Resists

- **Absorbance at 157 nm requires using thin resists**
  - Thin layers have more defects
    - Little data exists - risk unknown
    - How thin is "thin"?
  - Etch resistance questionable (hard masks offer solution)
  - EUV ultra-thin resist studies can provide useful data

- **New photochemical pathways imperil design chemistry**
  - Quantum yields of unwanted side reactions may begin to compete with photoacid generation (7.9 eV photon)
  - Undesired photochemistry can:
    - Increase the molecular weight which in turn lowers the dissolution rate and reduces the contrast
    - Decrease the molecular weight which can lead to volatile fragments and outgassing
    - Generate free radicals which may activate new chemical pathways that affect acid generation efficiency

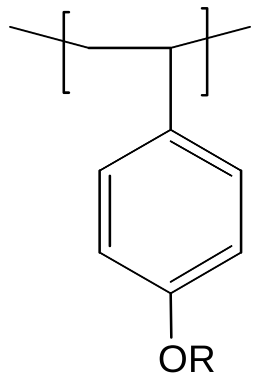
Difficulties in Using Existing Resists

Aspects of Using Existing Resists in Ultrathin Layers

- Are any current platforms more transparent at 157 nm?
- No manufacturing experience to assess defect-related yield loss or film defect metrology. Do pinholes even transfer?
- The whole resist is an interface!
  - substrate and atmospheric interactions critical
  - surface inhibition effects can have larger impact on performance than with thick resist
- Resist thinning must be better controlled
  - 2% thinning in a 700-nm resist becomes 20% in a 70-nm resist!
  - 20% thinning combined with limited aerial image will yield badly rounded profiles
- Etch resistance may be limited even for hard-mask pattern transfer

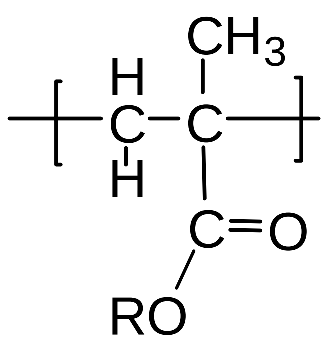
All Existing Polymer Platforms Require Thicknesses<70 nm

Phenolic



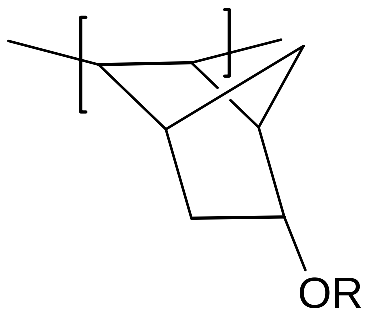
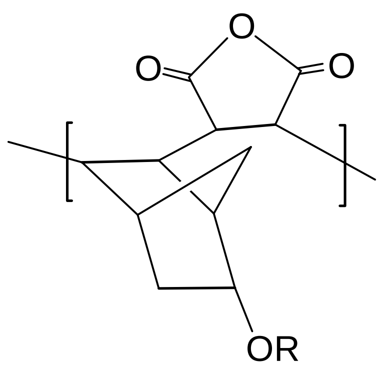
POLYMER	A /µm
Poly(styrene)	6.2
Poly(hydroxy styrene)	6.3
Commercial DUV resist A	7.3
Commercial DUV resist B	7.7
Commercial DUV resist C	8.3

Acrylic

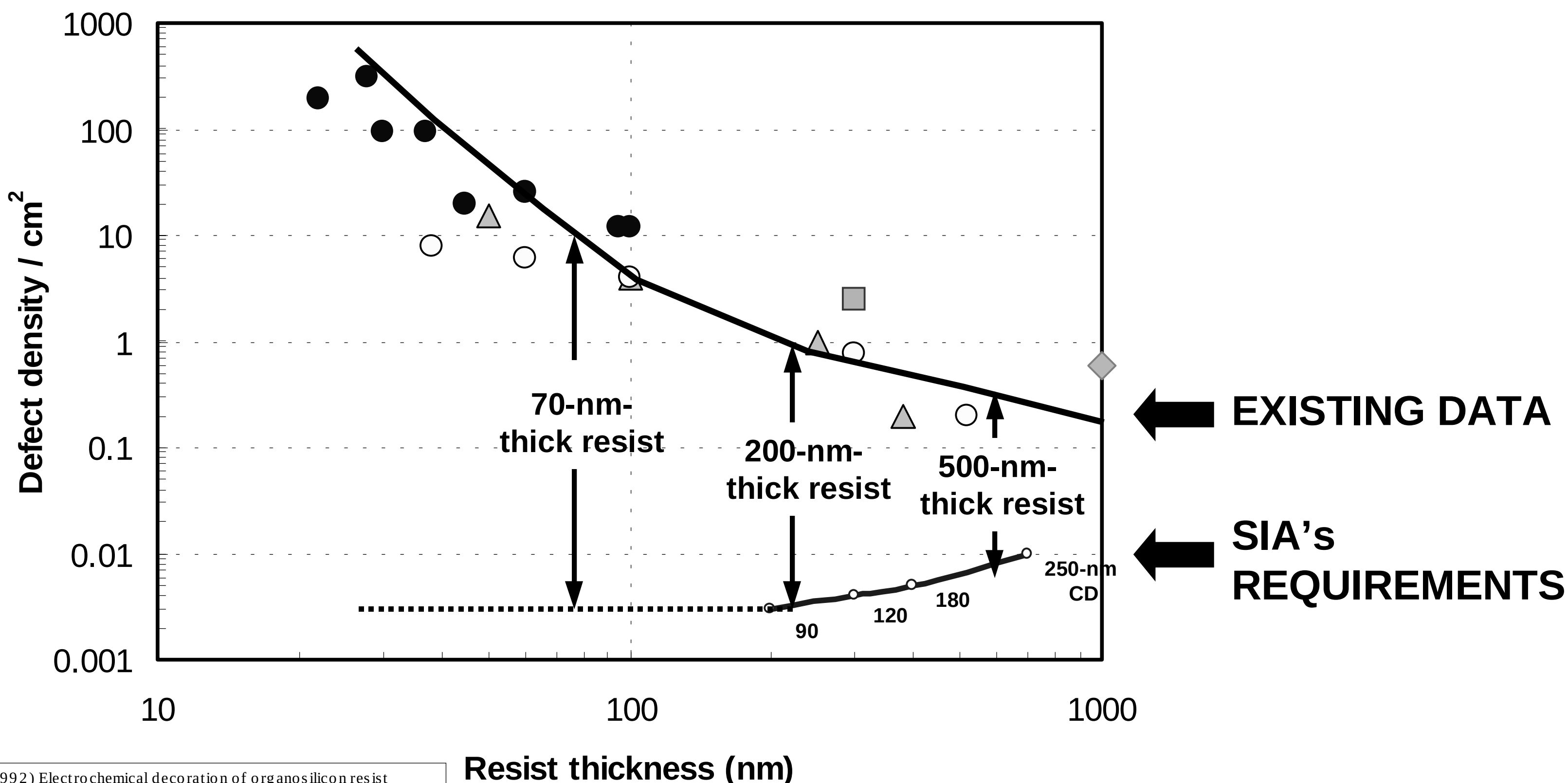


Poly(methyl methacrylate)	5.7
Poly(norbornyl methacrylate)	6.7
Poly(adamantyl methacrylate)	6.7
V1.1 terpolymer resin	7.4
Poly(isobornyl methacrylate)	7.6
V1.1 terpolymer resist	8.7
Poly(acrylic acid)	11.0

All Existing Polymer Platforms Require Thicknesses<70 nm

		POLYMER	A /μm
Norbornene		Poly(norbornene) (source A) Poly(norbornene) (source B) ROMP Poly(norbornene) Poly(norbornene) (source C)	6.2 6.8 6.8 7.1
Norbornene Maleic Anhydride		Commercial resist A Poly(norbornene-alt-maleic anhydride) A Poly(norbornene-alt-maleic anhydride) B	7.3 8.2 9.0

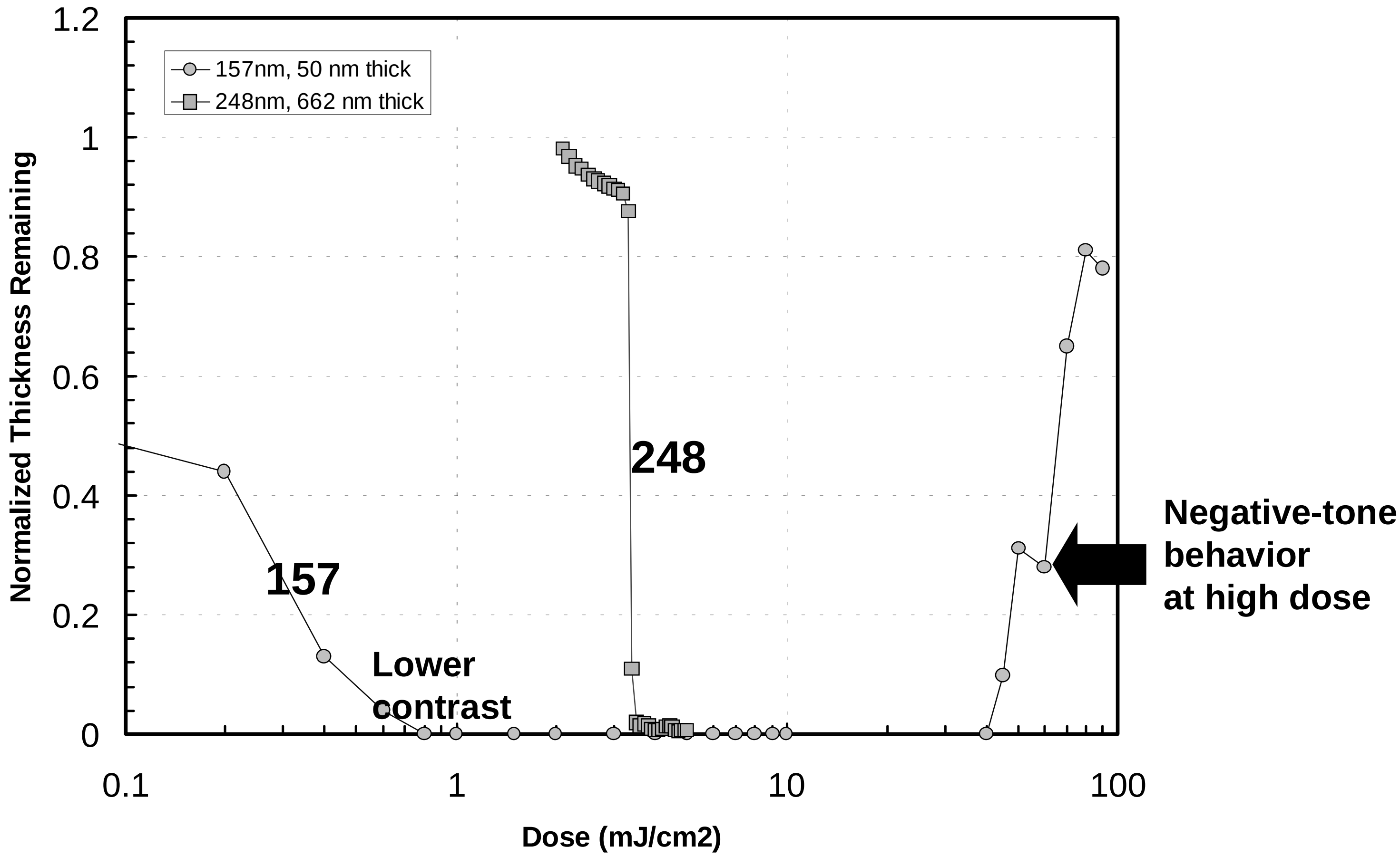
The Risk Of Using Ultrathin Resists: Defects!



- Kunz, MITLL (1992) Electrochemical decoration of organosilicon resist
- Muller, IBM (1992) Plasma decoration of organosilicon resist
- Early, AT&T (1992) Wet-etch decoration of organic resist
- Muller, IBM (1992) Plasma decoration of organic resist
- Kuan, Stanford (1988) Wet-etch decoration of organic resist
- 1997 SIA Roadmap

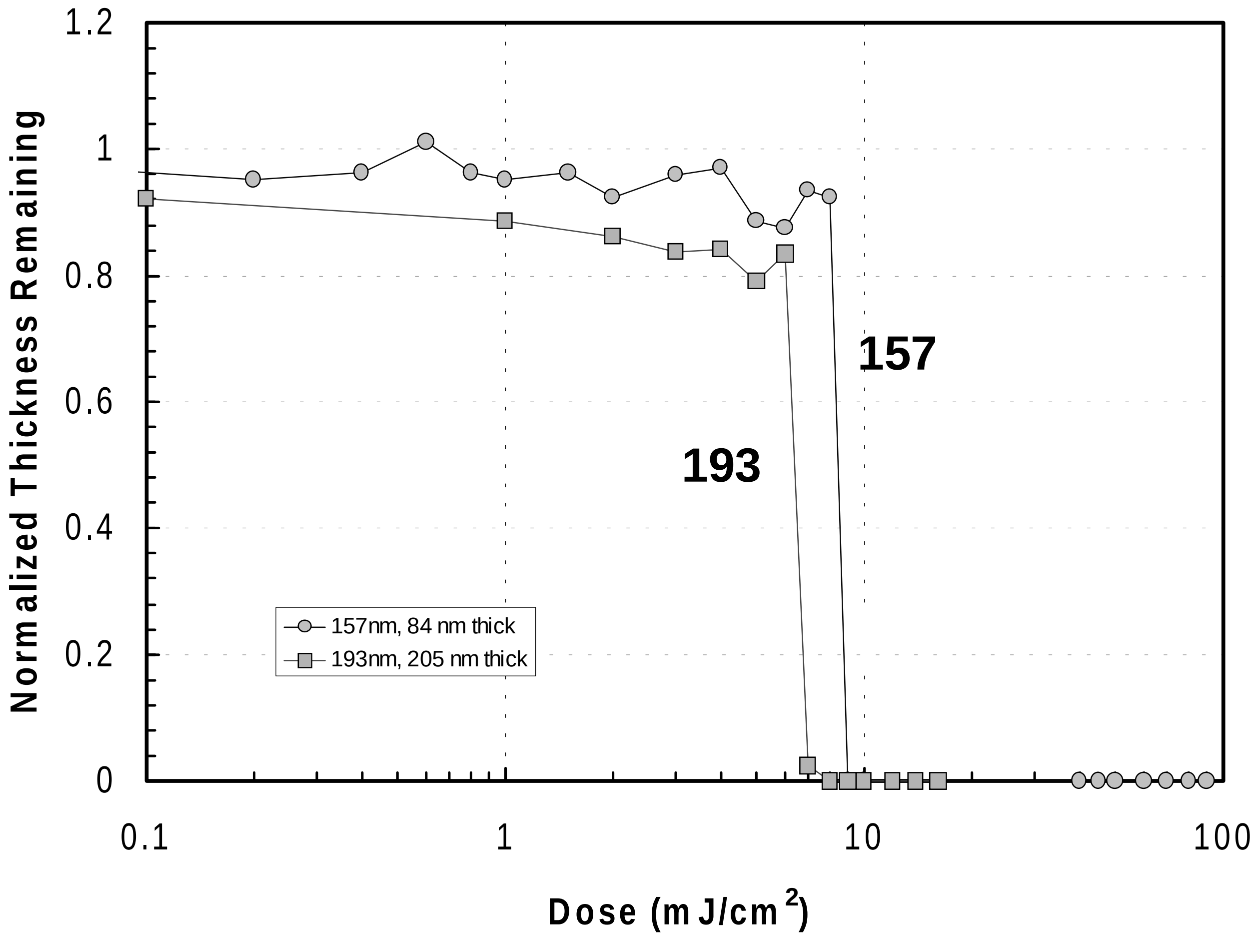
Risks associated with use of ultrathin resists in manufacturing are unknown.

Performance of a DUV Phenolic Resist: 157 nm vs. 248 nm



Even if thin layers are tolerable, acceptable lithographic performance is not ensured

Performance of a 193-nm Acrylic Resist: 157 nm vs. 193 nm



Summary of contrast curve study

Seven resists tested to date:

Resist	Type	Polymer	E_0 (mJ/cm^2)	E_0^{157} (mJ/cm^2)	γ	γ_{157}	Thinning (nm/min)	Neg dose (mJ/cm^2)
A	248	PHOST	3.4	0.8	**79**	**1**	48	50
B	193	Acrylic	14	9.0	7	10	30	>90
C	193	CO-MH-Ac	8.0	2.5	**9**	**3**	54	>90
D	193	Acrylic	7.5	9.0	8	12	18	>90
E	193	CO-(MH)	4.0	9.0	6	8	4	>90
F	193	Acrylic	7.0	2.0	2	3.3	18	>90
G	ebeam	PHOST	NA	4.0	NA	2	NA	NA

- **All resists tested (at 248, 193, or 157 nm) on bare silicon with their thicknesses adjusted to yield film ODs of ~0.4.**
- **All development times shortened to 15 seconds.**

Use of Existing Resists

How it Might Look Based on Current Data

- Cyclo-olefin or acrylic 193-nm resist
- Absorption coefficient requiring a thickness of 55 nm
- Sensitivity <10 mJ/cm^2
- Contrast >8
- Yet unresolved:
  - Etch resistance
  - Outgassing (thin layer may help some)
  - Reflection control
  - Defects
- Unresolved issues not critical to "tool testing resist"
- Inorganic ARC/hardmask would address etch resistance and reflection control
- Improved silicon-containing bilayers may also help

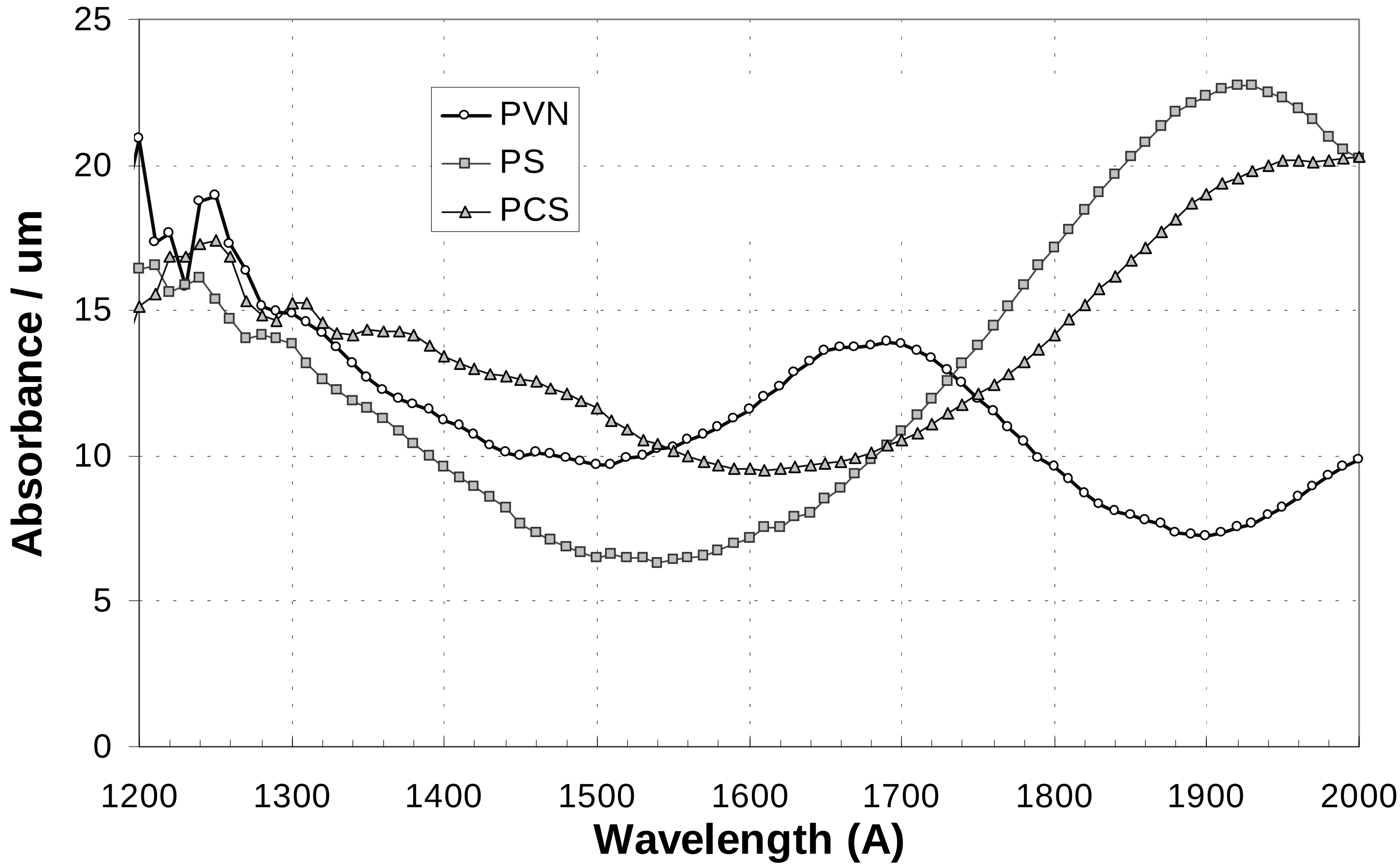
Photoacid Generator Absorbance

Photoacid Generator (PAG)	Added absorbance to a 200-nm-thick resist with 4 wt% PAG
Naphthylimidotriflate	0.05
Triphenylsulfonium perfluorobutane sulfonate	0.17
Bis(t-butylphenyl)iodonium camphor sulfonate	0.14

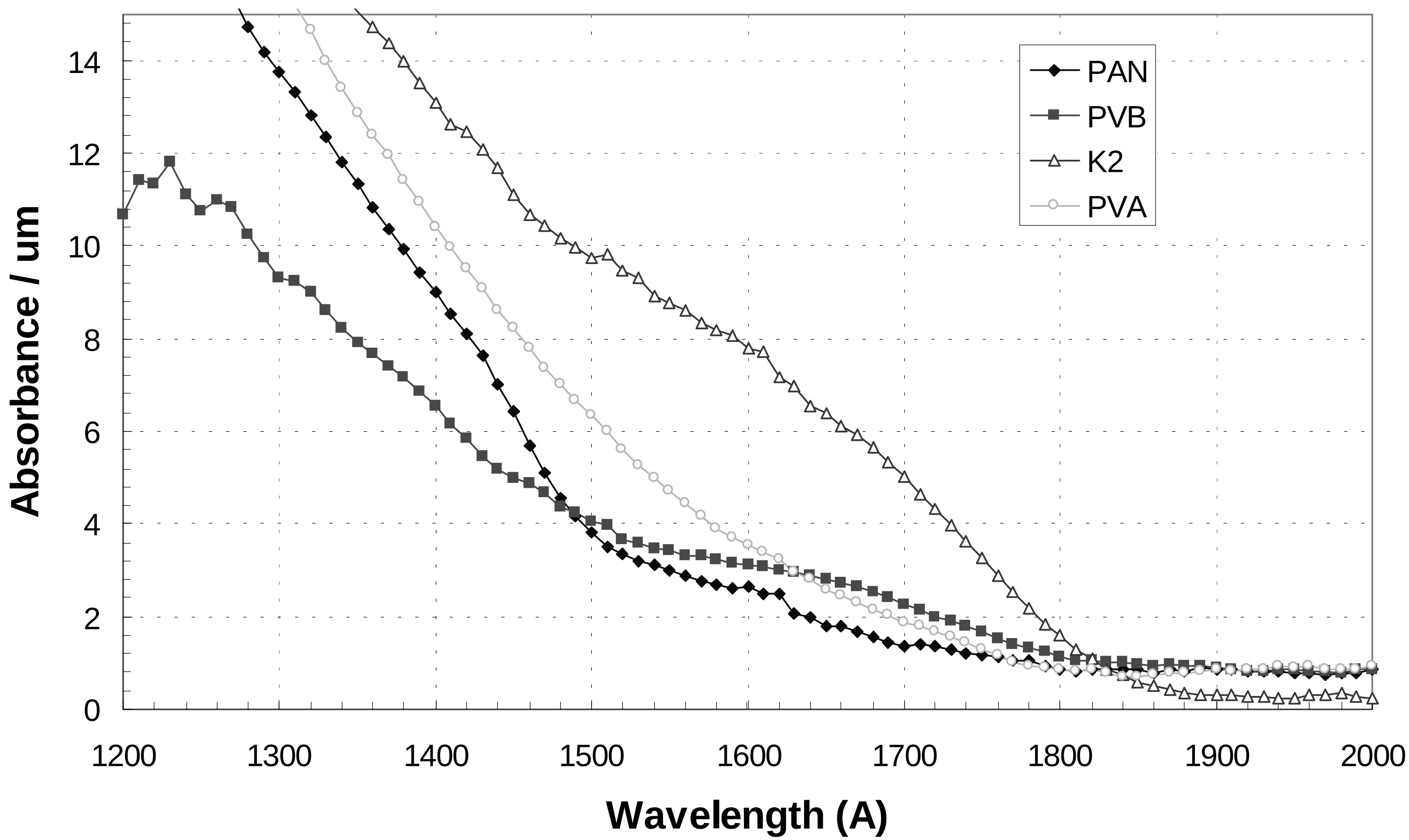
Note: Aromatic PAGs are more transparent at 157 than at 193.

VUV absorbance of common polymers

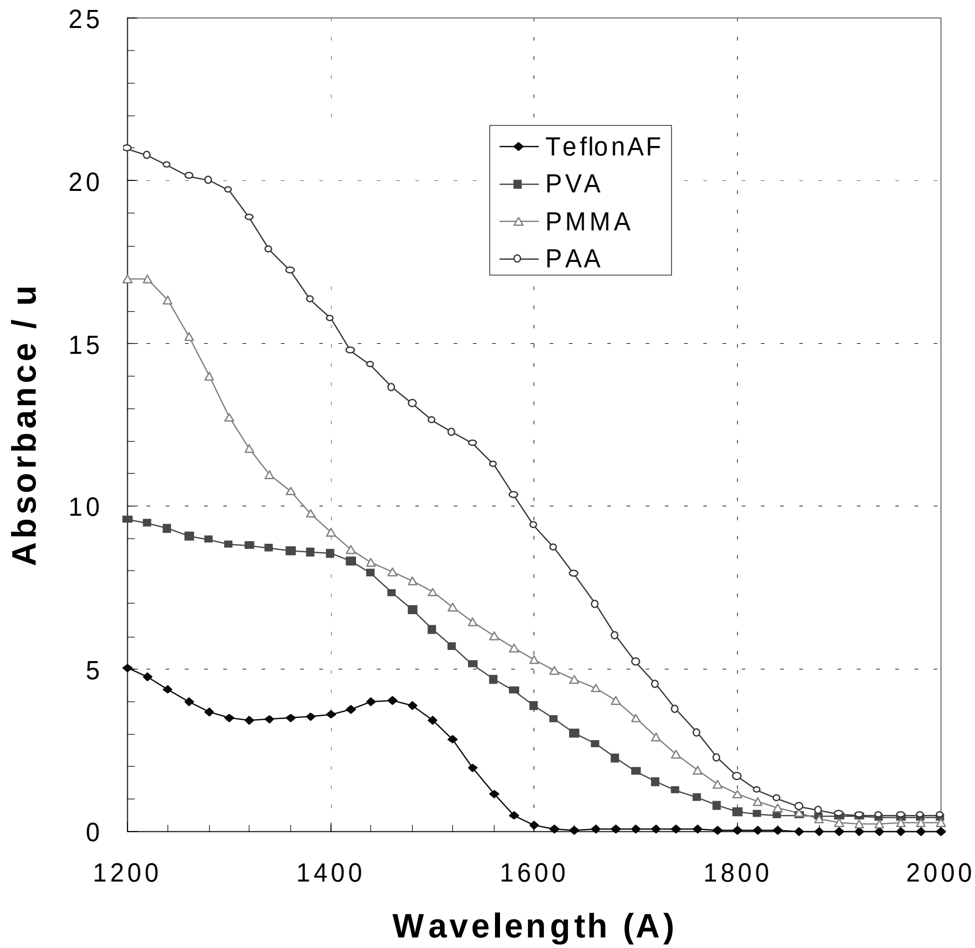
Poly(vinylaromatics): Absorption-band shifting for 157 nm?



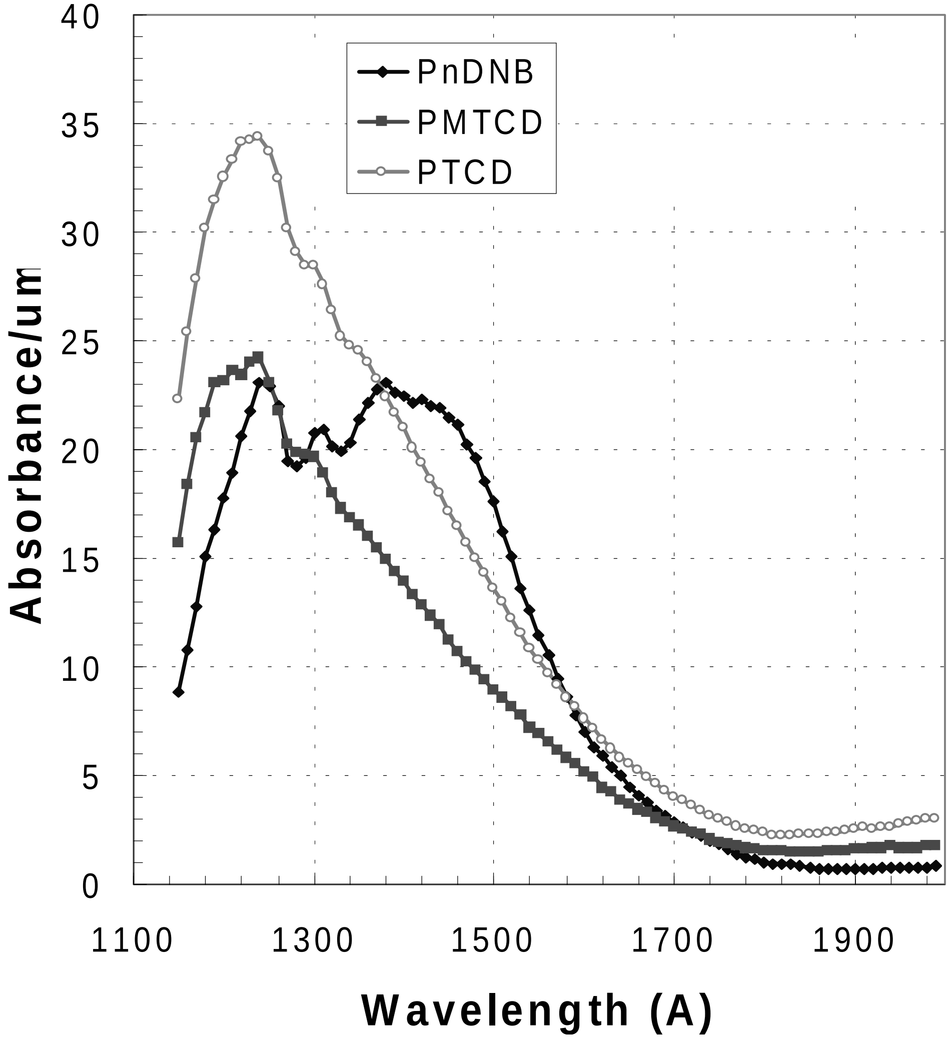
Aliphatic polymers



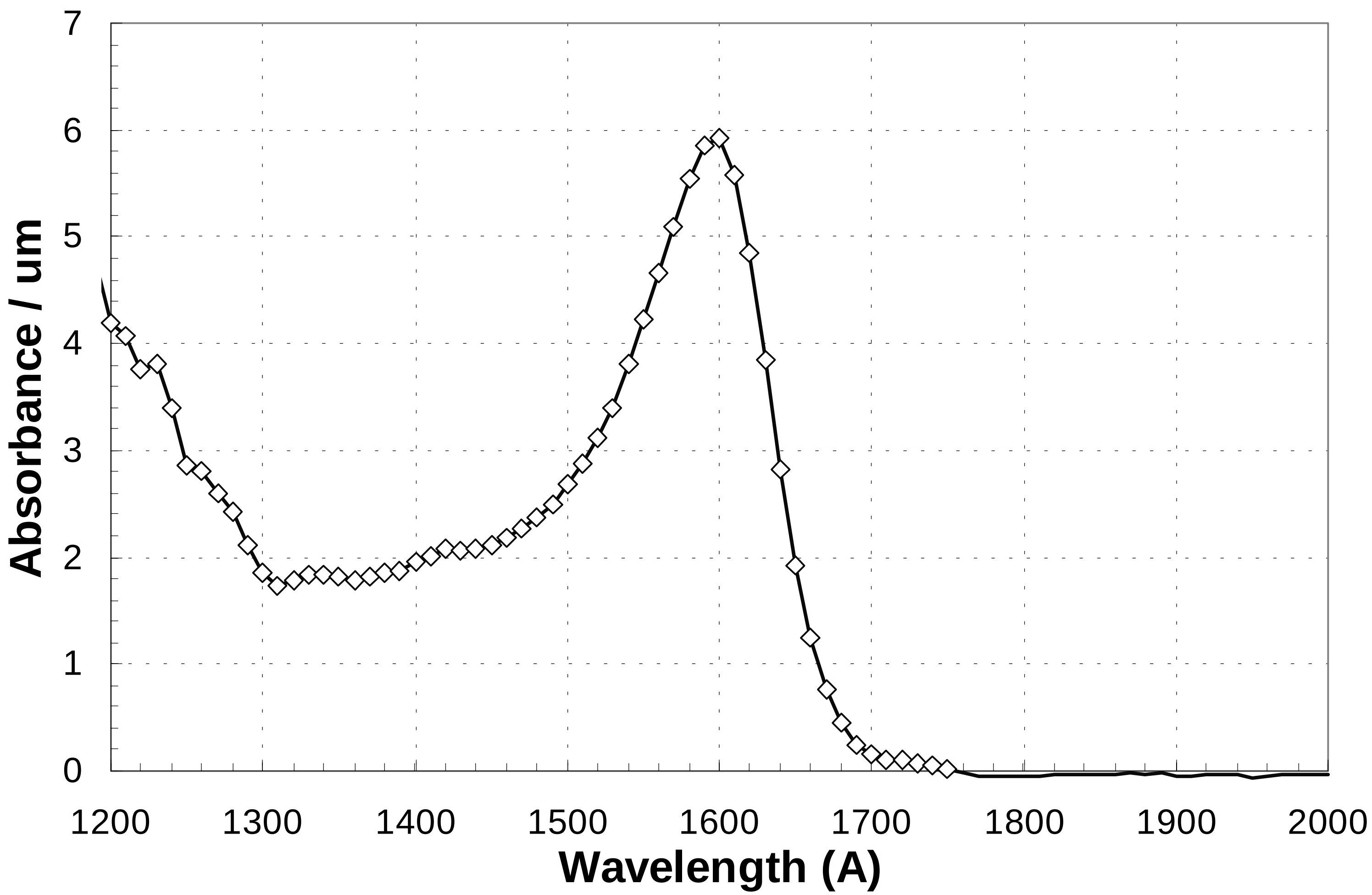
Aliphatic polymers



Cyclo-olefins

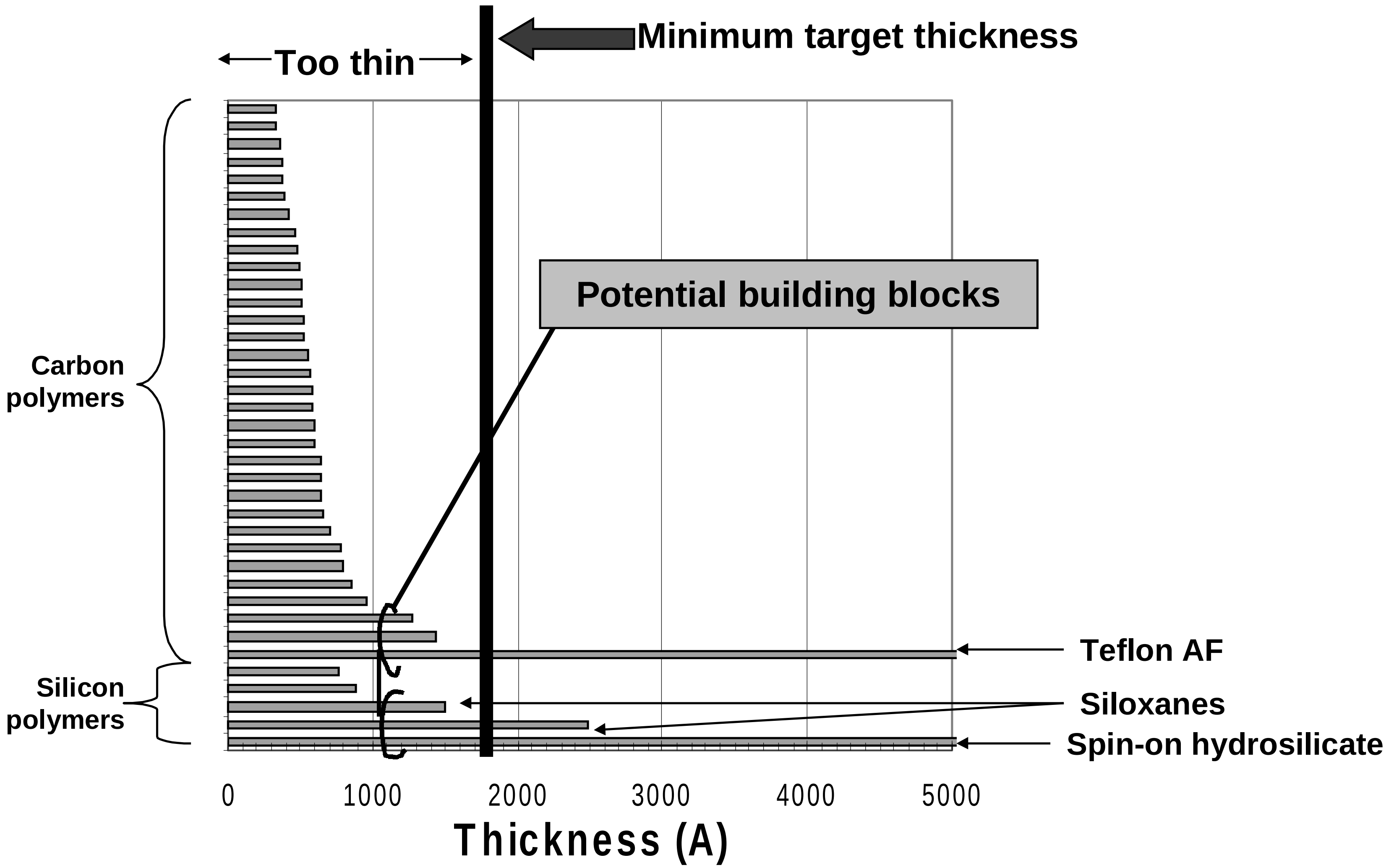


Nafion

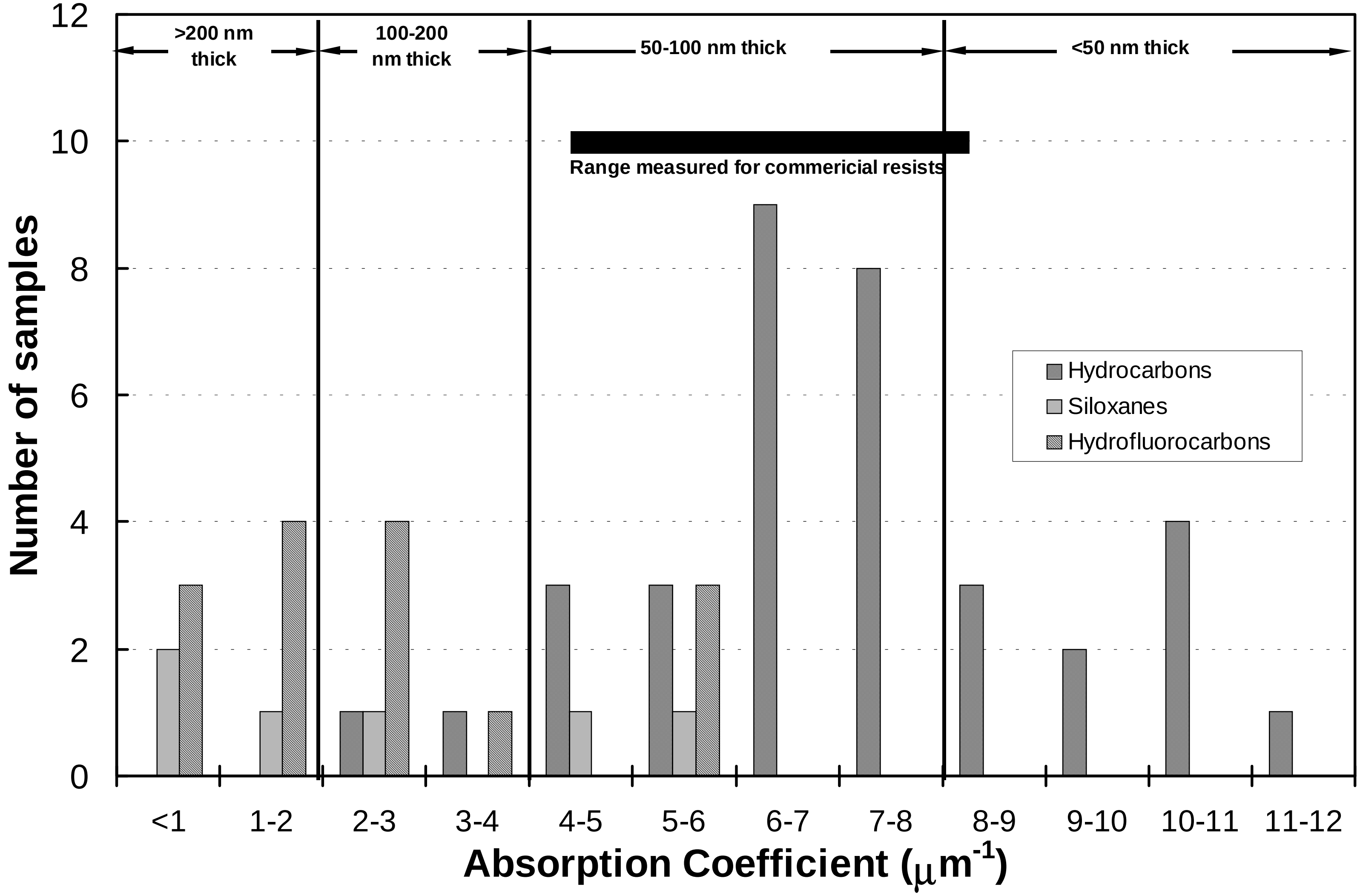


Absorbance / um
7
6
5
4
3
2
1
0
1200
1300
1400
1500
1600
1700
1800
1900
2000
Wavelength (A)

Polymer thicknesses required for an optical density of 0.4



Absorption Summary For Polymers Tested



What prospects for new materials have been identified?

Routes to More Transparent Polymers

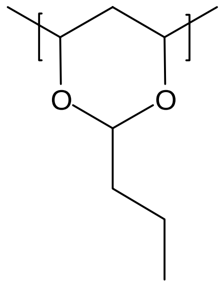
- Carbon polymers can be made more transparent by “dilution” via transparent comonomers or side chains
  - siloxane functionality is best candidate, although fluorocarbons and polyethers are possible as well
- Avoid all π electrons (i.e., no double bonds)
- C-C σ-bond can be made more transparent through addition of transparent electron withdrawing groups (i.e. fluorine)
  - large impact on dissolution and possibly adhesion
  - transparencies yielding films >200 nm are possible
- C-C σ-bond can also be made more transparent (to a limit) by controlling the bond conformation
  - little impact on dissolution and adhesion
  - limited gains in absorbance
- Judicious manipulation of these approaches should yield a material that can be used in thicknesses of ~200 nm

Modification of Existing Platforms With Transparent Functionality

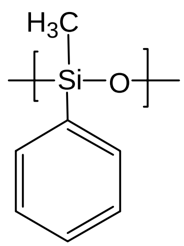
RESIN	A / μm	THICKNESS (OD=0.4)
Methacrylate Resist A	7.5	53
Methacrylate Resist B	8.7	46
Siloxane-modified methacrylate resist	4.6	87
Perfluoroalkyl methacrylate polymer	4.7	85

- **In order to compensate for the carbonyl absorbance, the substituents must be very transparent, i.e. CF_x and SiOR. This alters solubility significantly.**
- **Only modest gains in thickness possible (this applies to all existing resist platforms).**

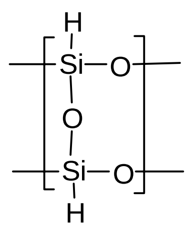
Examples of Transparent Materials



Poly(vinyl butyral)
A = 3.2/μm
L = 125 nm (OD=0.4)

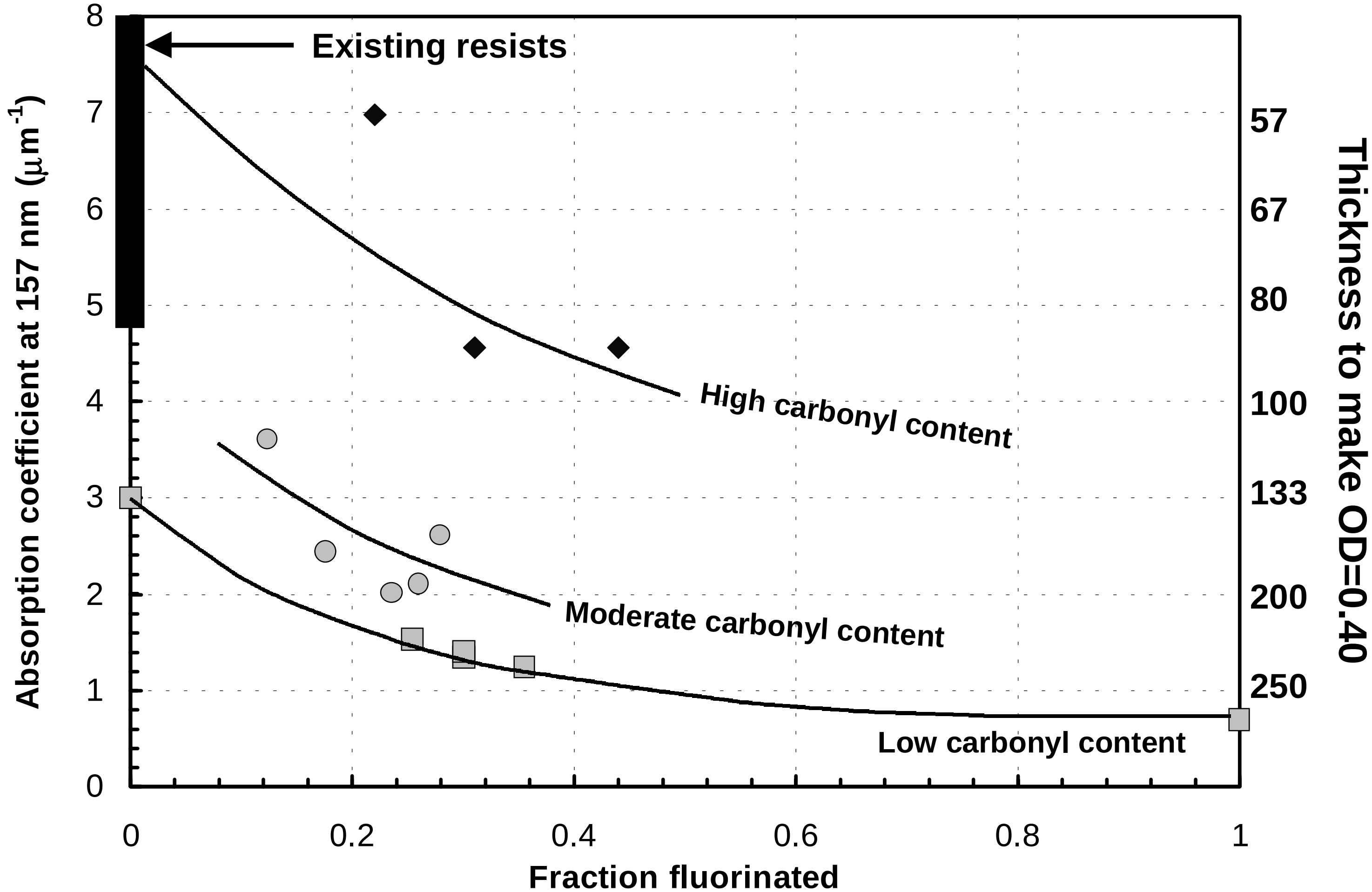


Poly(phenylmethyl siloxane)
A = 2.7/μm
L = 148 nm (OD=0.4)



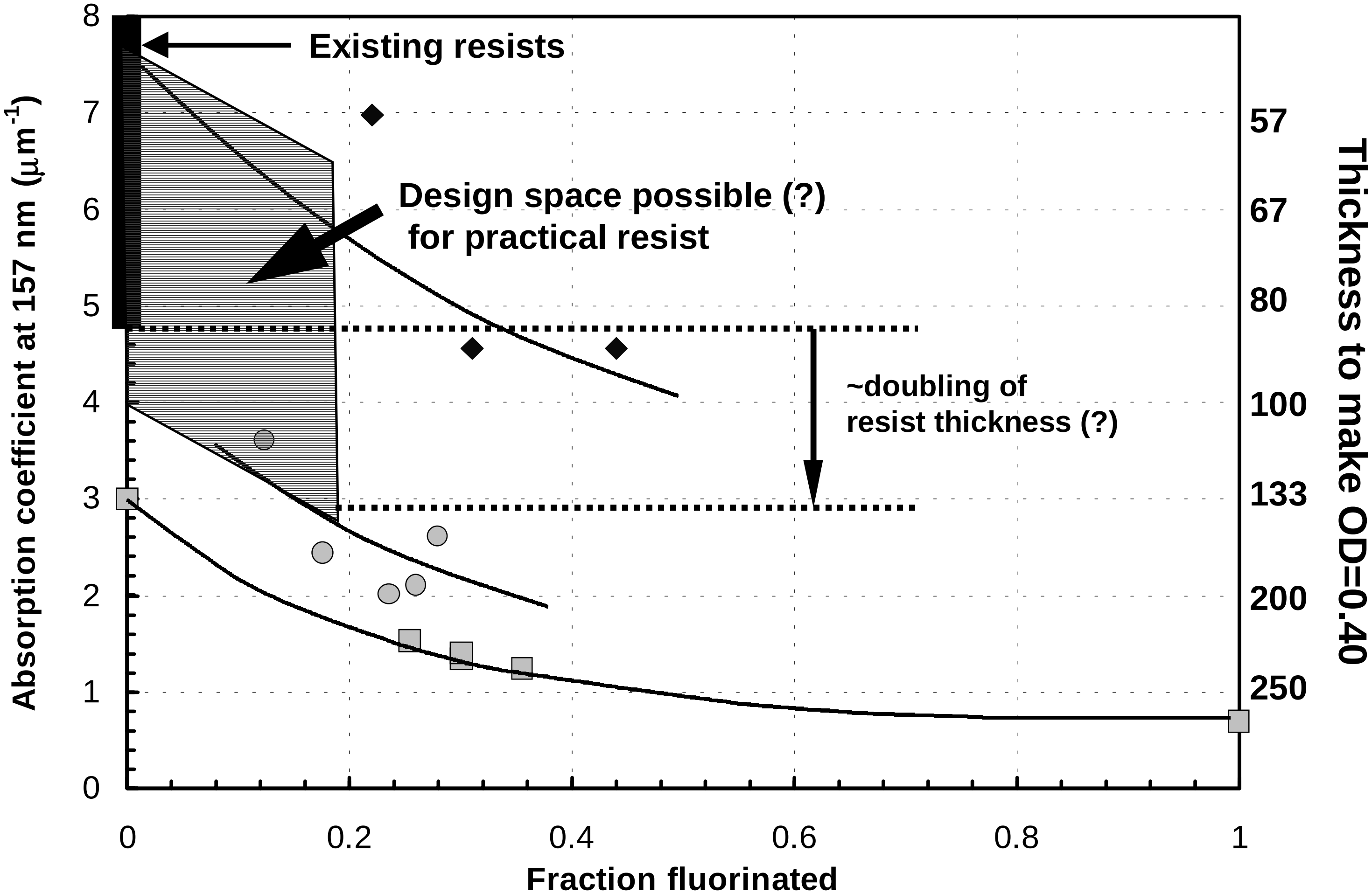
Poly(hydrosilsesquioxane)
A = 0.02/μm
L = 20 μm (OD=0.4)

Strong Levers On Absorbance: Fluorocarbon And Carbonyl Content



(Lines drawn to guide the eye)

Design Space Possible (?) By Optimal Manipulation Of Fluorine And Ester Content



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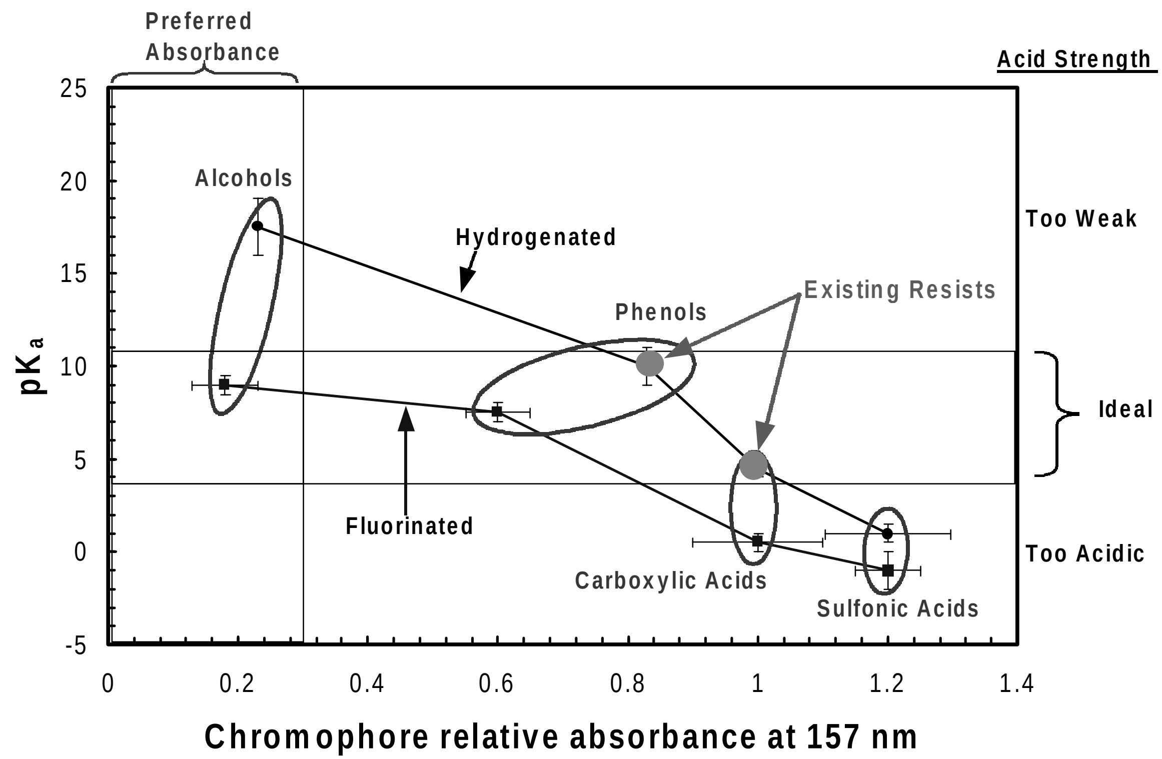
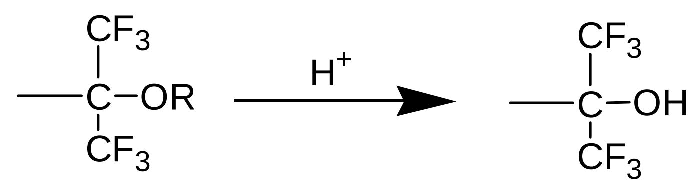
Fluorine-Activated Alcohols Offer Route to Transparency and Base Solubility



π-electron-free base solubilizing group (Hoechst, 1992)



Routes to 157-nm Resists

- **Existing hydrocarbon resists will be applicable for thicknesses < 80 nm**

- **Slight modifications to existing resists should afford thicknesses between 80 and 110 nm**
  - **Siloxyl-functionalized resist an obvious route to bilayer resist**
  - **Simply putting hexafluoropropanol-protected groups on existing resists should yield transparencies in this area**

- **No base soluble <u>and</u> transparent homopolymers exist to obtain resist thicknesses > 100 nm**
  - **Copolymerization is required to obtain desired resin**
  - **A combination of approaches will be necessary for >150 nm**

    Siloxyls, hexafluoropropanols, copolymerization, etc.

Outgassing as a Design Concern

- Quantum yields for volatile product formation have been measured for many polymers at 253.7 nm
  - poly(t-butyl acrylate) has Φ=0.083 for isobutene liberation*
  - isobutene primary product observed in t-butyl ester resists (assisted by acidolysis)
  - rates at 157 nm may be even higher
- Open frame exposure experiments conducted at Lincoln have shown some t-butyl ester resists measurably thin during exposure to 157 nm (unlike 193 and 248 nm)
- The Lincoln/Sematech resist outgassing CRDA has shown that deposition of outgassed products occurs more efficiently in a nitrogen ambient, which is unique to 157 nm
- Resist-related contamination should constitute an up-front concern to the tool and resist designers

*Reinisch and Gloria, 1968

Summary

- **An existing commercial resist should be suitable as a tool-testing resist**
  - Selection criteria based on combination of absorbance and lithographic performance at 157 nm
  - Maximum thickness ~90 nm
  - Further work (defects, etch resistance, integration) needs to be done to use in manufacturing, but EUV effort should help

- **Opportunities exist to develop new materials**
  - Absorbance at 157 nm still dominated by molecular transitions, and hence new chemistries can afford greater transparency
  - It appears to be a balancing act between absorbance, solubility characteristics, and etch resistance
  - C-F and Si-O functionality should play key roles
  - Large synthesis effort needed to make headway (including even basic structure-property studies)

Acknowledgments

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