Ultraviolet Deposition of Thin Films and Nanostructures

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Nanostructured Metal Oxide Thin Films

Venue: Yorkshire Bank North (First Floor), Ricoh Arena, Coventry, CV6 6GE

Date: Thursday 18th October 2012

www.vacuum-uk.org

Outline of Talk

1. Principles & properties of UV Excimer Lamps

2. Development of UV deposition system

3. Potential Applications:

    Surface engineering
    Oxide, metal deposition
    Interface engineering
    Nanoparticle deposition & doping

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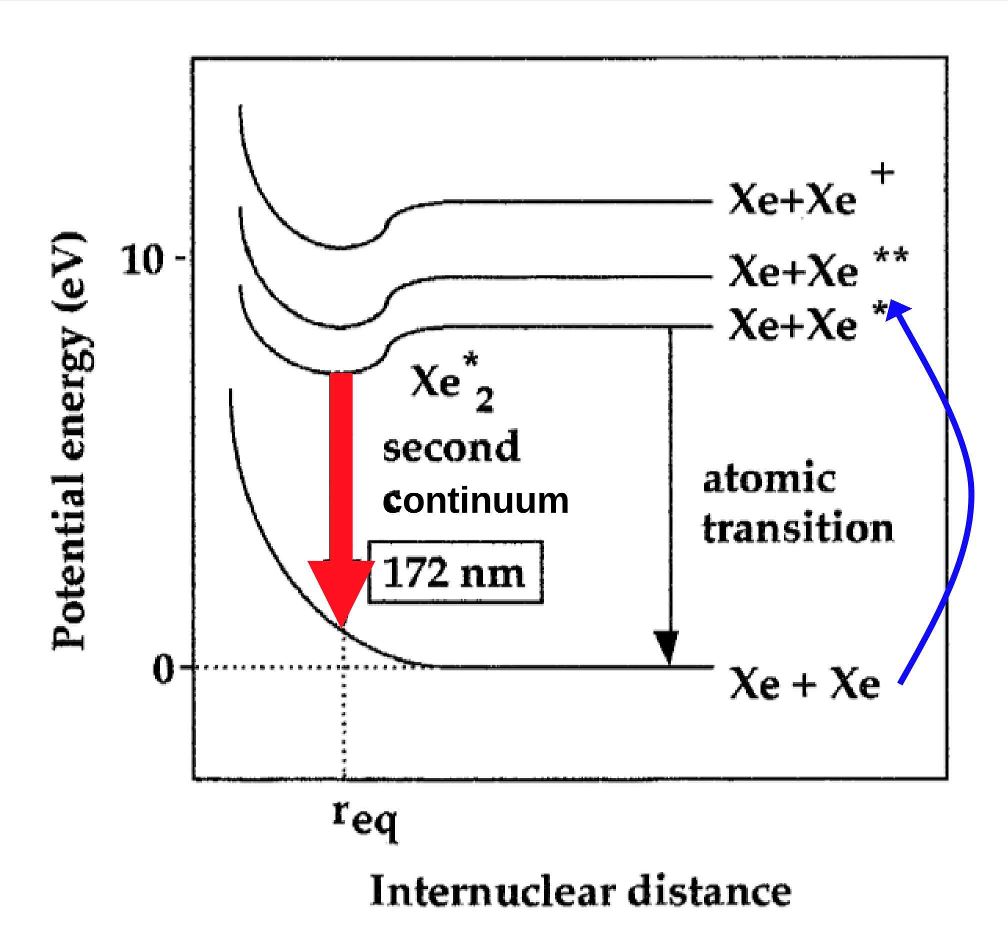
Excimer Excitation Schematic: Rare Gas (R_g)



Xe atoms excited by energetic es to higher electronic states & even ionised

Excimer (Excited Dimer) molecules formed by collision

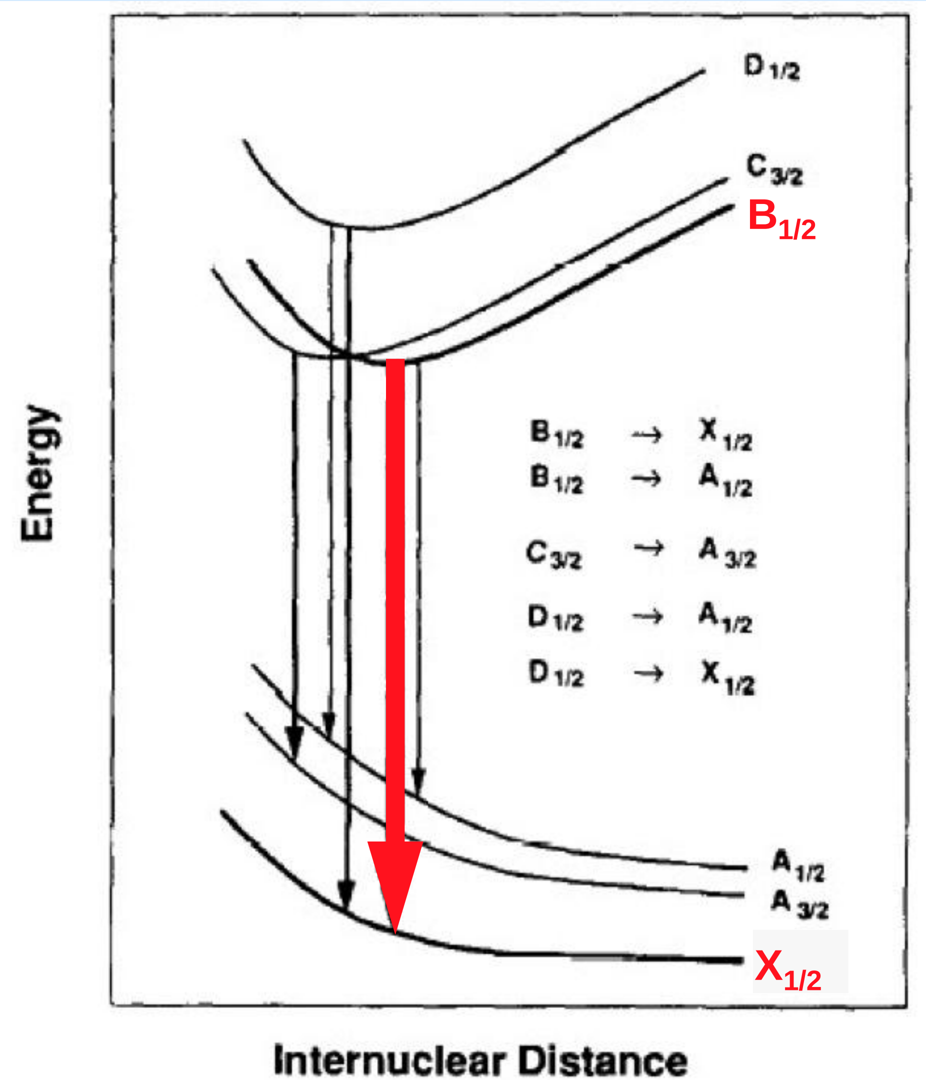
Excimer relaxes by collisions and photon emission to ground state

$$e^- + Rg \rightarrow Rg^* + 2e^-$$
$$e^- + Rg \rightarrow Rg^+ + e^-$$
$$Rg^+ + 2Rg \rightarrow Rg_2^+ + Rg$$
$$Rg_2^+ + e^- \rightarrow Rg^{**} + Rg$$
$$Rg^* + Rg + Rg \rightarrow Rg_2^* + Rg$$
$$Rg_2^* \rightarrow 2Rg + h\nu(UV)$$

Ground state:

- **Dissociation to original atoms**
- **Non-absorbing to the light produced**
- **Atoms are “Renewable”**
- **Non-polluting chemistry**

Exciplex Excitation Schematic: Rare Gas Halide (R_gX^*)



Rg	X	RgX* $D_{1/2} \rightarrow X_{1/2}$	RgX* $B_{1/2} \rightarrow X_{1/2}$	RgX* $C_{3/2} \rightarrow A_{3/2}$	RgX* $B_{1/2} \rightarrow A_{1/2}$	RgX*
Ne	F	106	108	110	111	~ 145
Ar	F	185	193	203	204	290±25
Ar	Cl		175		195	245±15
Ar	Br		165	172	183	
Kr	F	220	248	275	272	400±35
Kr	Cl	200	222	240	235	325±15
Kr	Br		207	222	228	~ 318
Kr	I		190	195	225	
Xe	F	264	351	460	410	610±65
Xe	Cl	236	308	345	340	450±40
Xe	Br	221	282	300	325	440±30
Xe	I	203	253	265	320	~375

High energy electron excitation & ionisation

$$e^- + Rg \rightarrow Rg^* + e^-$$

$$e^- + Rg \rightarrow Rg^+ + 2e^-$$

$$e^- + X_2 \rightarrow X + X^-$$

3-body recombination or harpooning reaction

$$Rg^+ + X^- + M \rightarrow RgX^* + M$$

$$Rg^* + X_2 \rightarrow RgX^* + X$$

Exciplexes unstable (ns lifetime) & emit UV or quench (low P)

$$RgX^* \rightarrow Rg + X + h\nu(UV)$$

$$RgX^* + X_2 \rightarrow Rg + 3X$$

or trimer formation (high P)

$$RgX^* + 2Rg \rightarrow Rg_2X^* + RG$$

Summary of “Excimer” UV Sources

Excimer	λ (nm)	E (eV)	UV range
NeF^*	108	11.48	
Ar_2^*	126	9.84	
Kr_2^*	146	8.49	VUV
F_2^*	158	7.85	
$ArBr^*$	165	7.52	
Xe_2^*	172	7.21	
$ArCl^*$	175	7.08	
KrI^*	190	6.49	
ArF^*	193	6.42	
$KrBr^*$	207	5.99	
$KrCl^*$	222	5.58	
KrF^*	248	5.01	
XeI^*	253	4.91	UV-C
Cl_2^*	259	4.79	
$XeBr^*$	283	4.41	
Br_2^*	289	4.29	UV-B
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I_2^*	342	3.63	
XeF^*	351	3.53	UV-A

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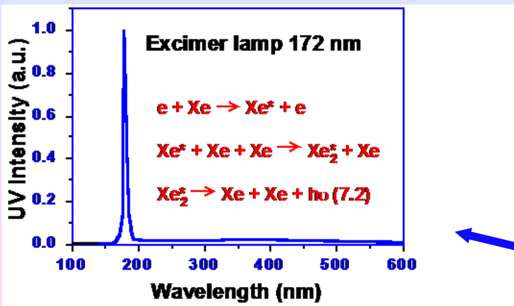

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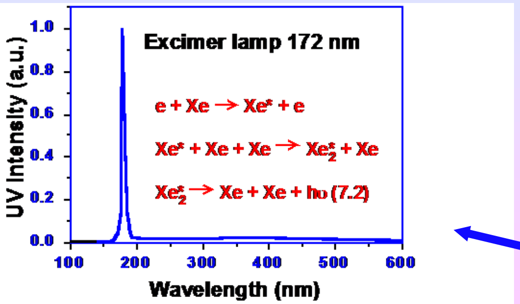

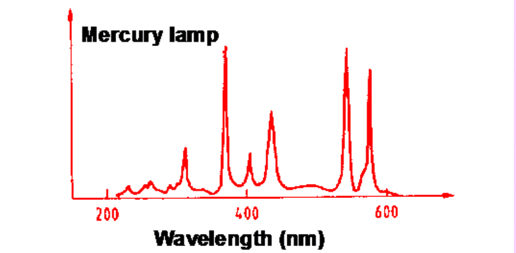

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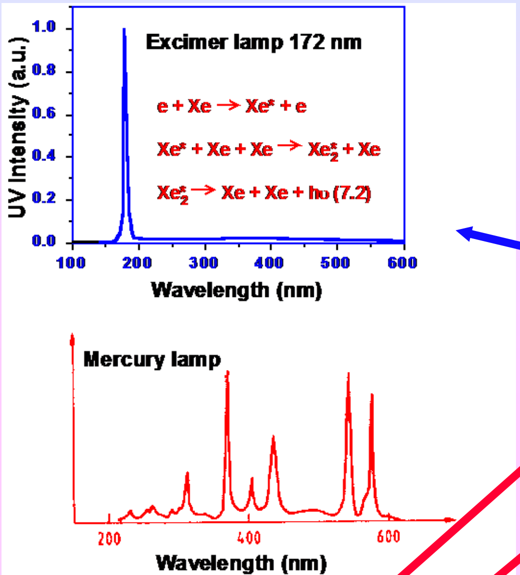

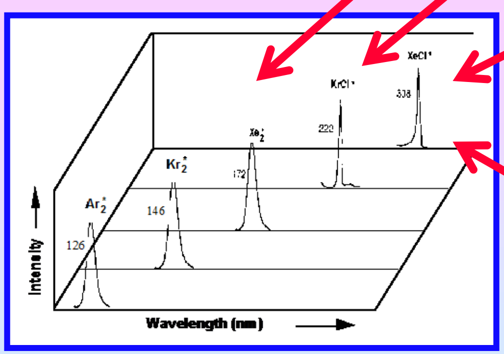

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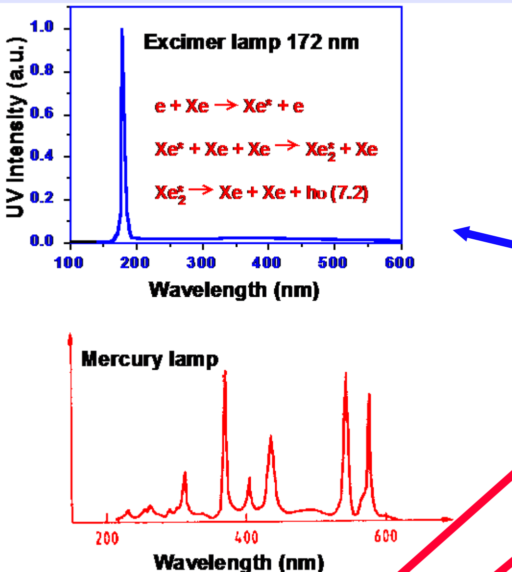

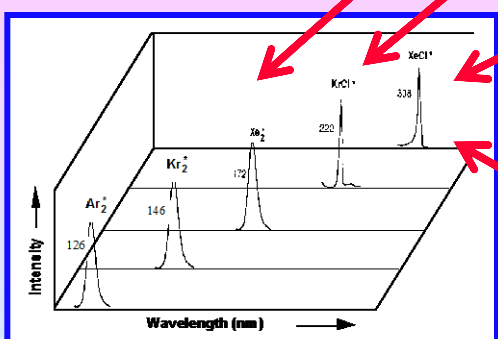

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Common Excimer Lasers

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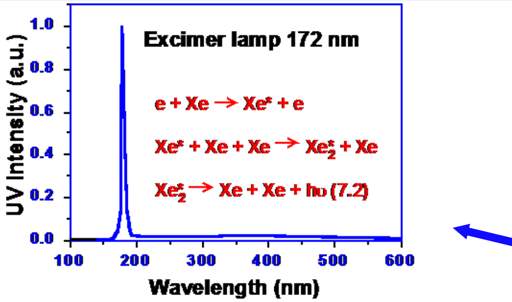

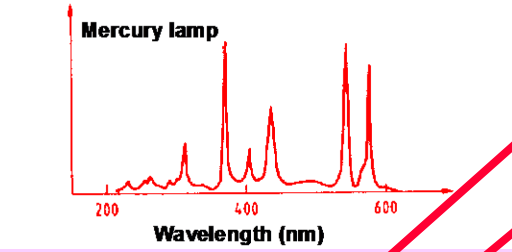

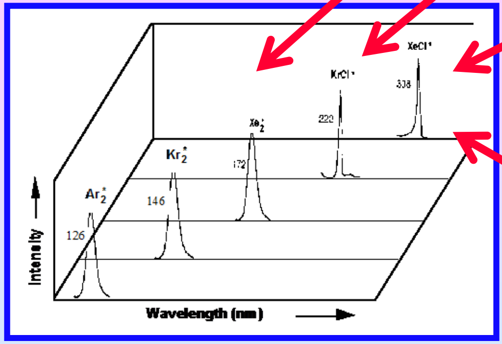

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Common Excimer Lasers

V E R Y

Expensive !

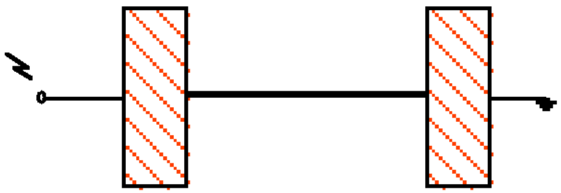
Classical v. Dielectric Barrier Discharges

Classical v. Dielectric Barrier Discharges

V E R Y Cheap !

Classical v. Dielectric Barrier Discharges

V E R Y Cheap !



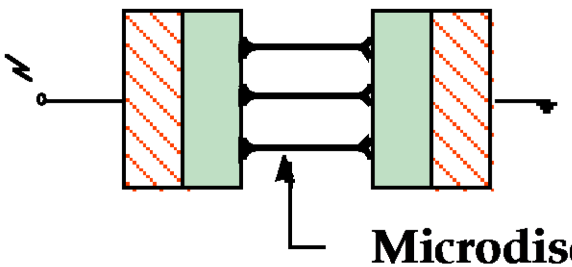
Classical discharge

Problems:

- High current
- Electrode sputtering
- Contamination of discharge gas

Metal Electrode

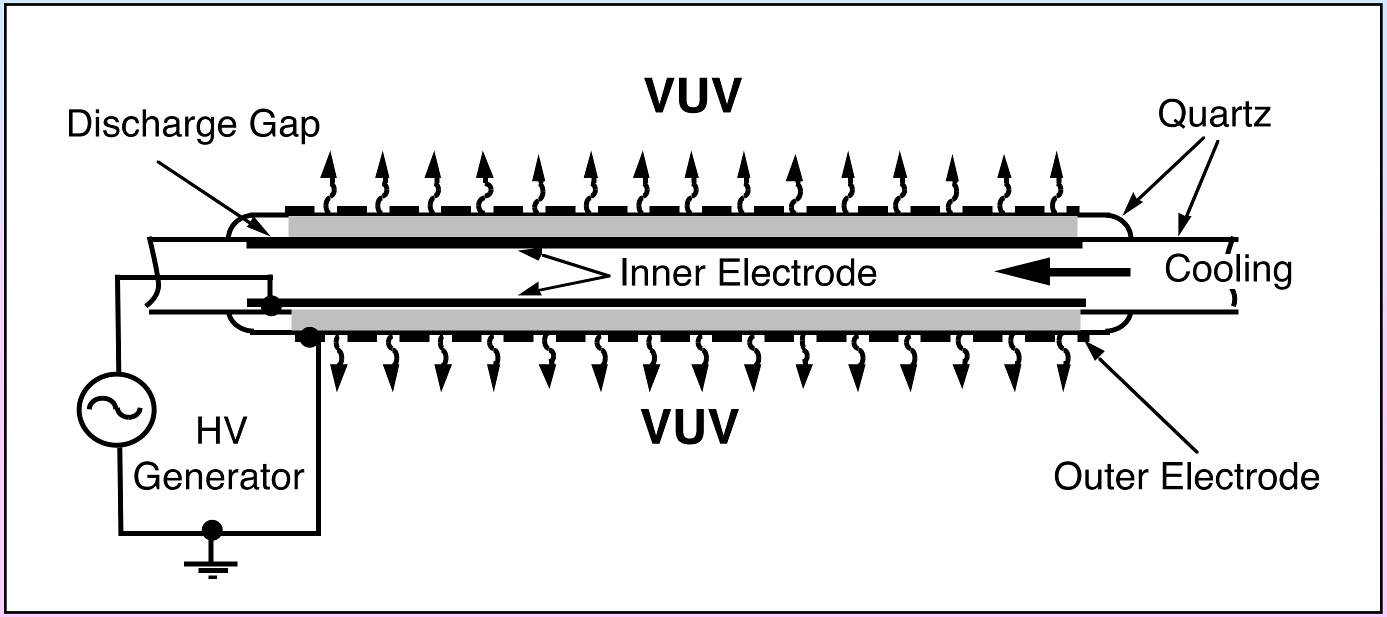
Dielectric barrier

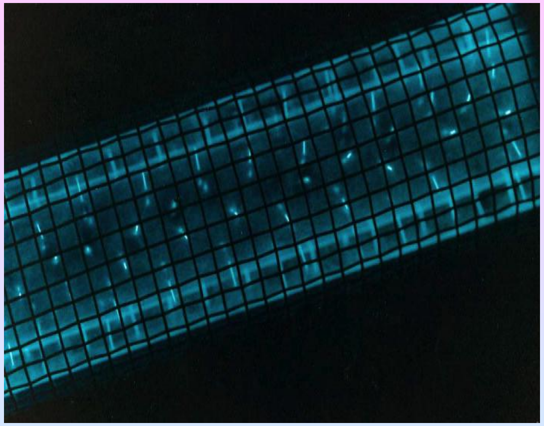


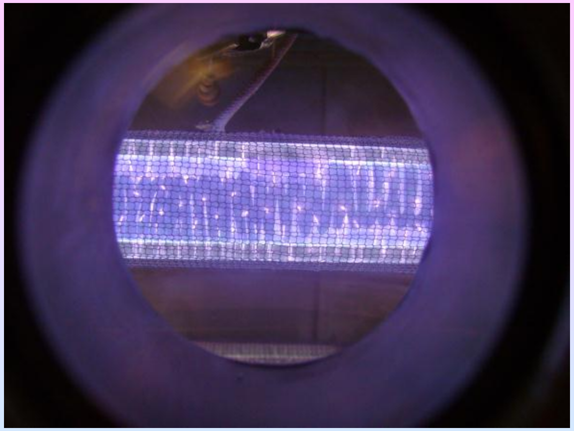
Dielectric barrier discharge

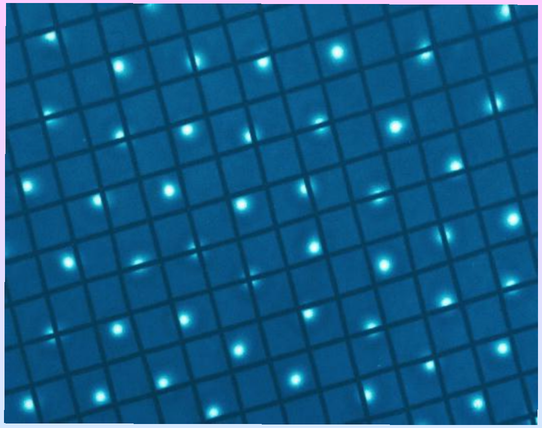
Microdischarge in discharge gap

Cylindrical Excimer UV Source

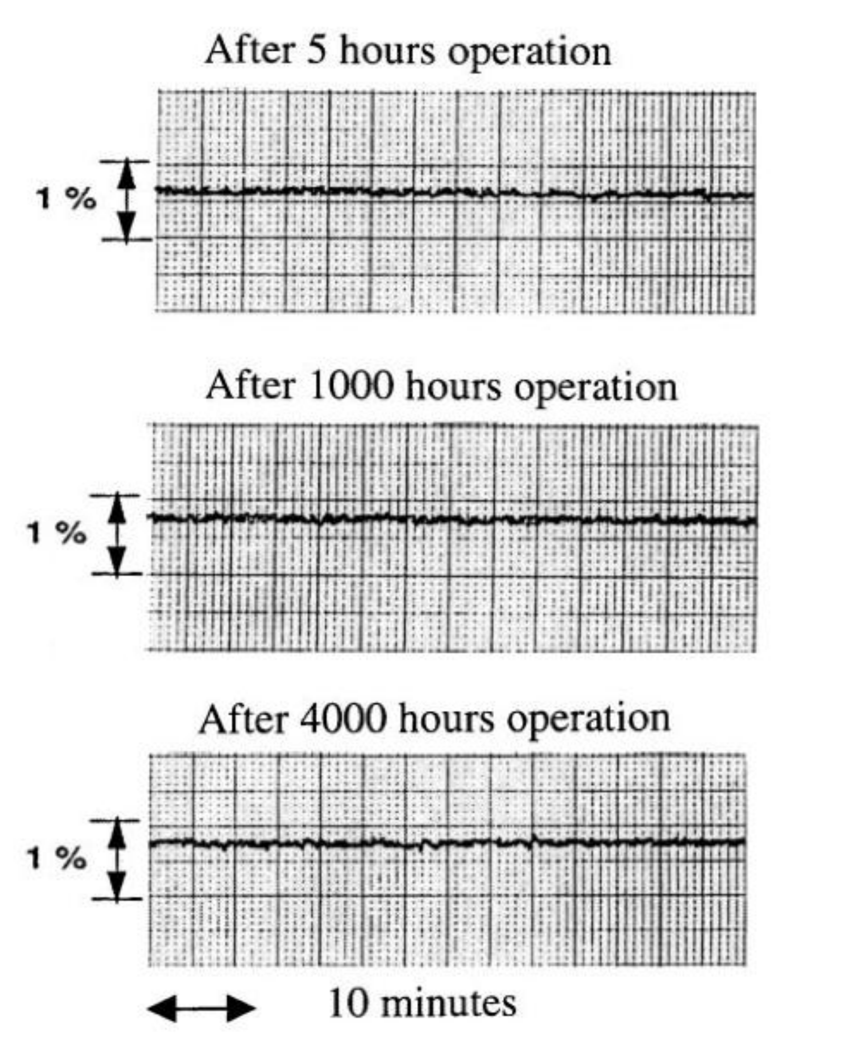


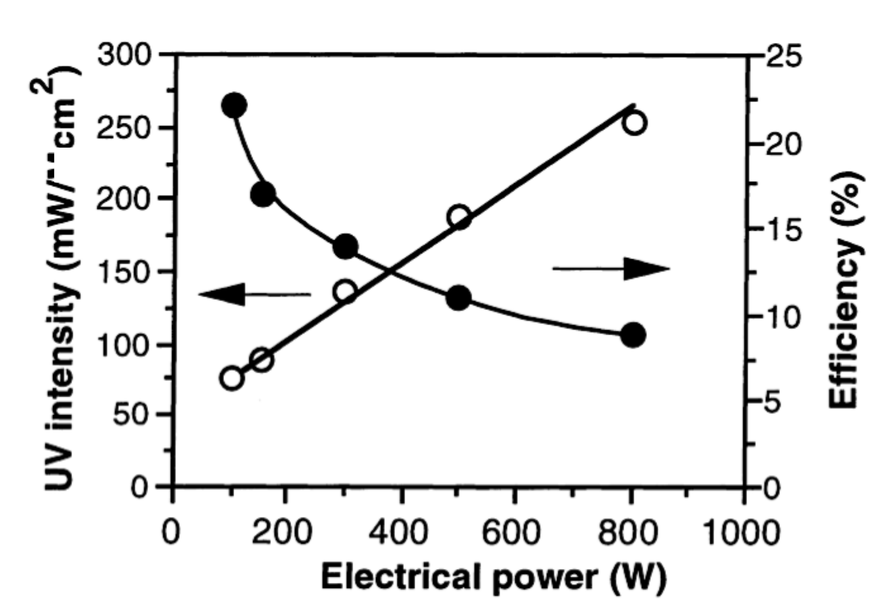


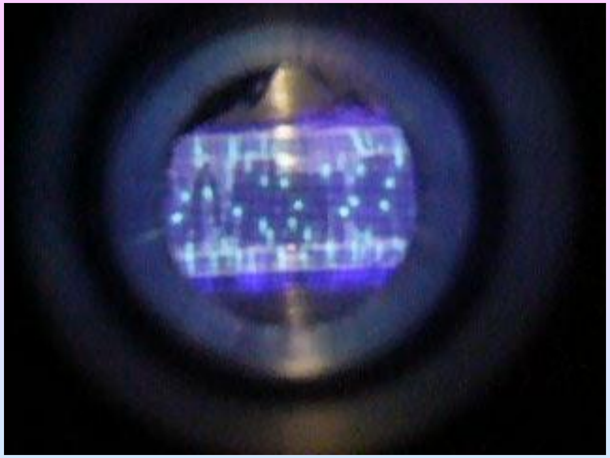




Efficiency & Long term stability: 222nm



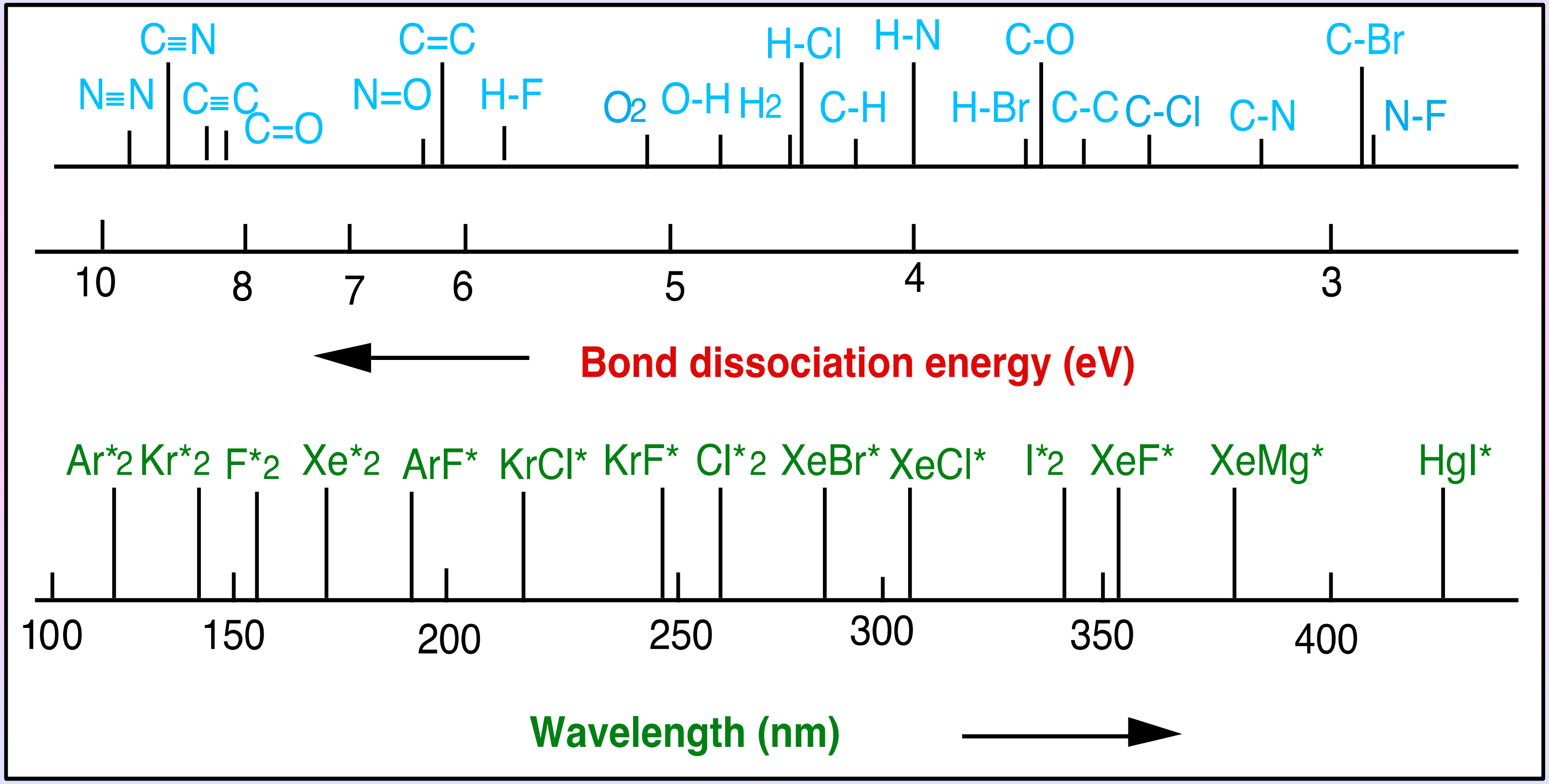




Excimer lamp: Characteristic features

- Incoherent, almost monochromatic, more than 20 wavelengths, high UV and VUV intensities
- Robust and inexpensive, ecologically beneficial (Hg free)
- Long stable lifetime
- No self-absorption, high efficiency
- Easy to handle, no major cooling
- Scalable - large areas possible (cm^2-m^2)……..

Bond Dissociation Energy of Covalent Bonds and Wavelengths of Excimer UV Radiation



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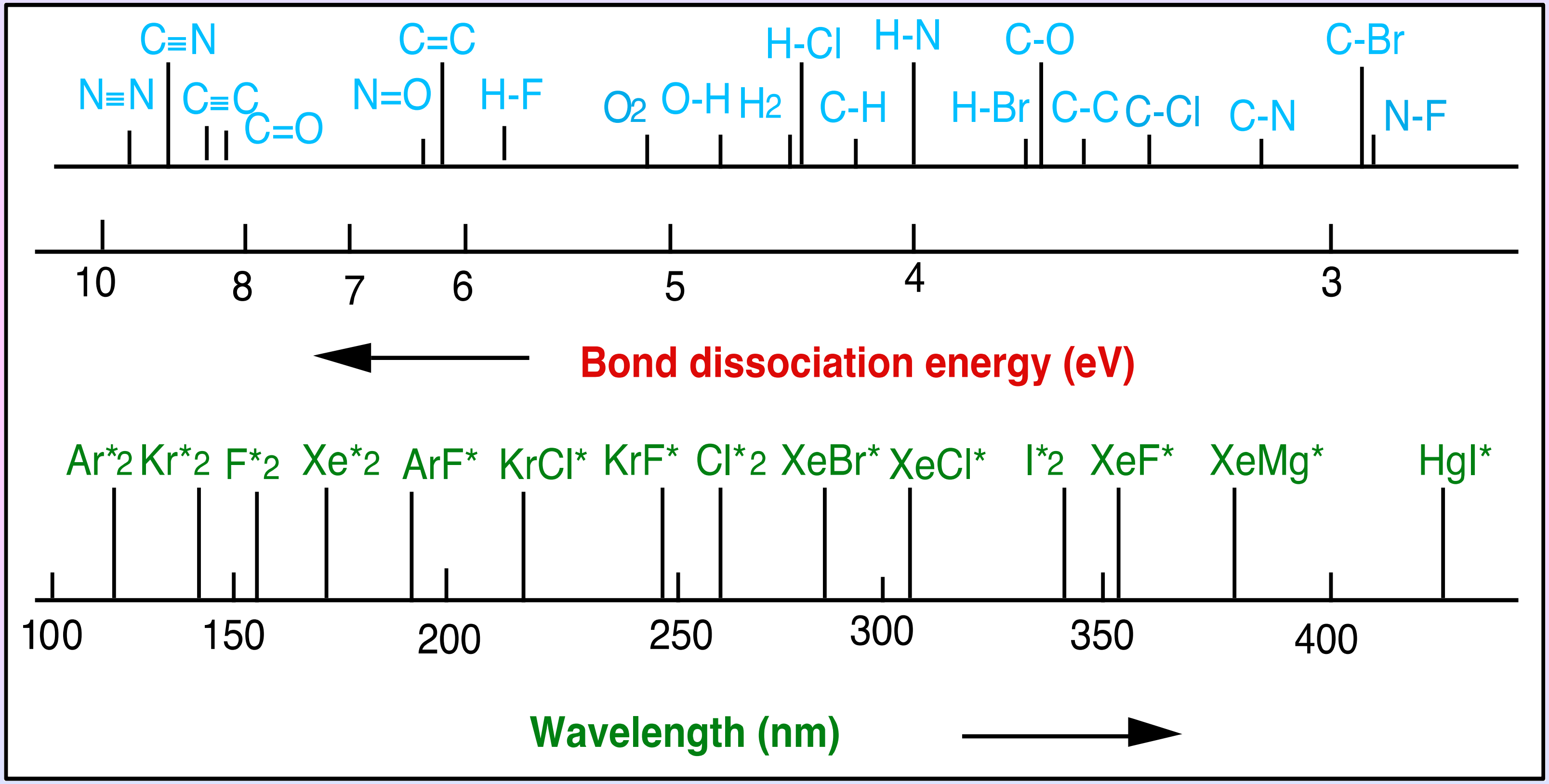

….lots of available photochemistry !

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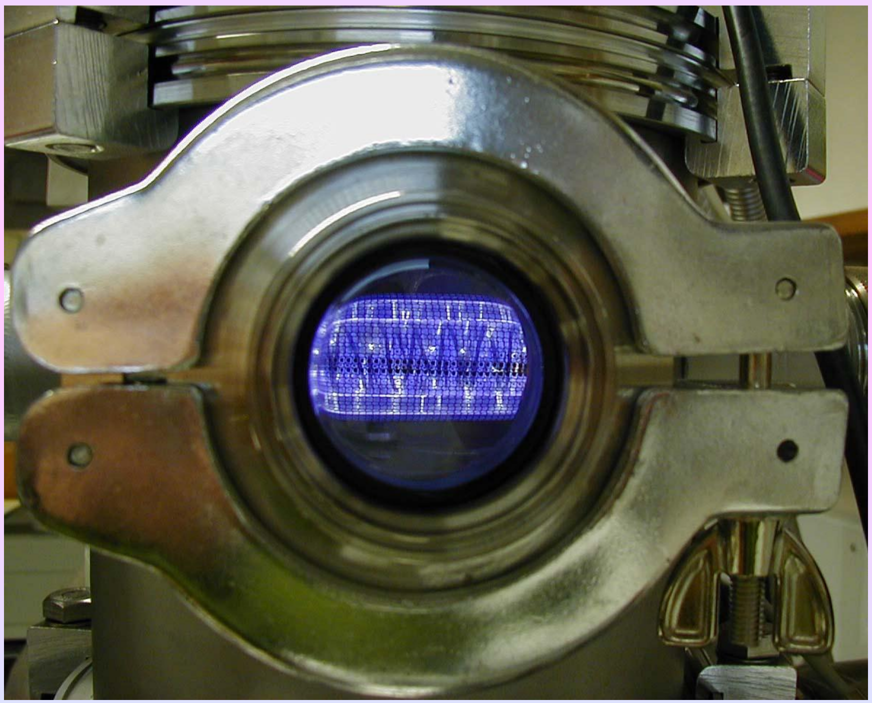
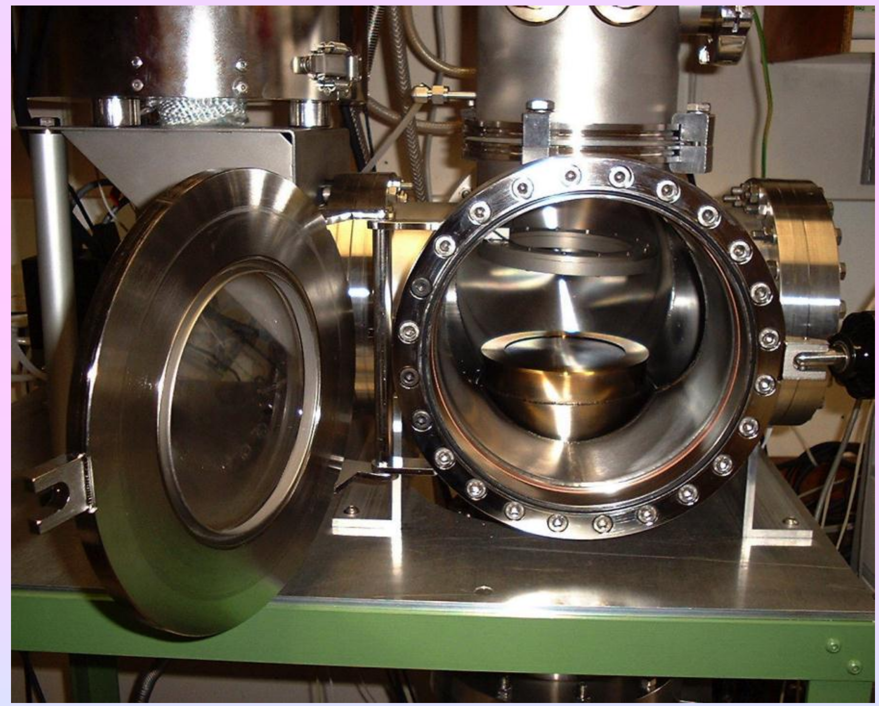
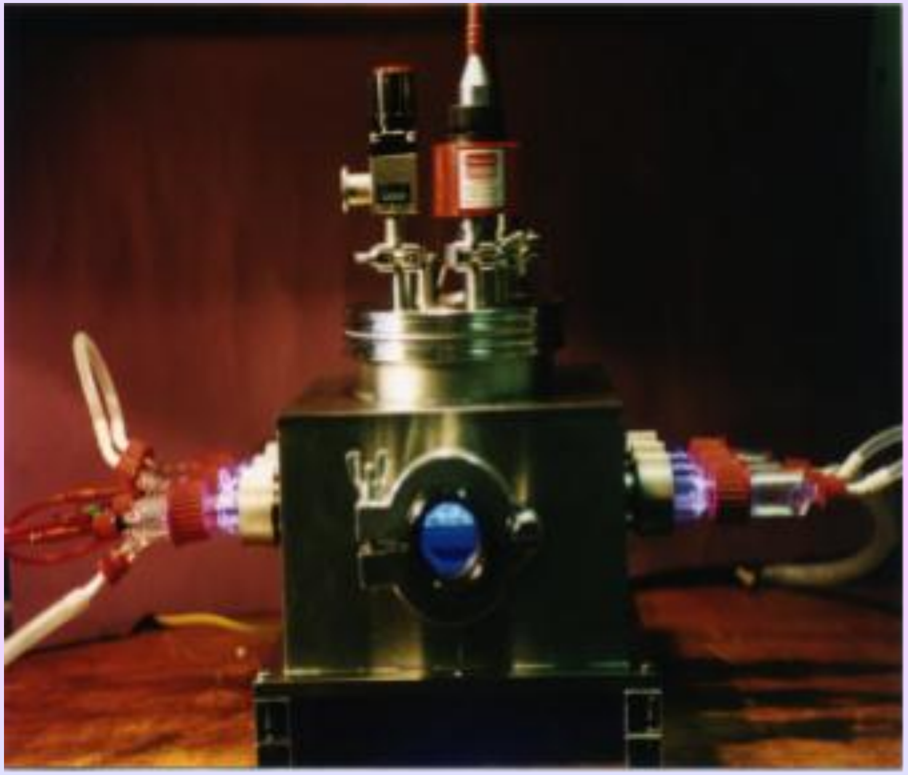
Lamp Chamber

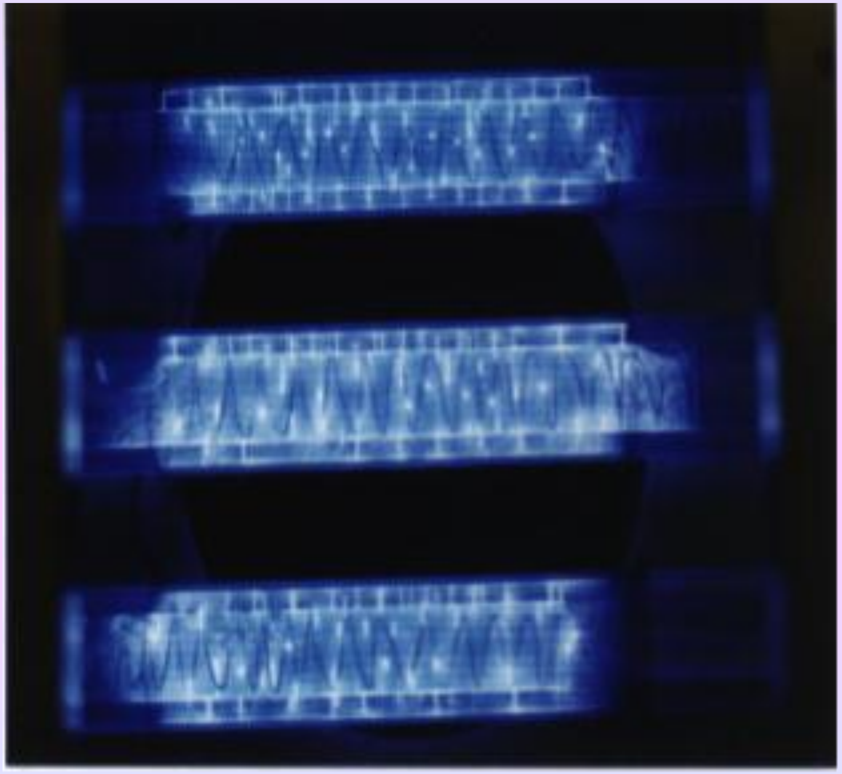


Reactor Chamber

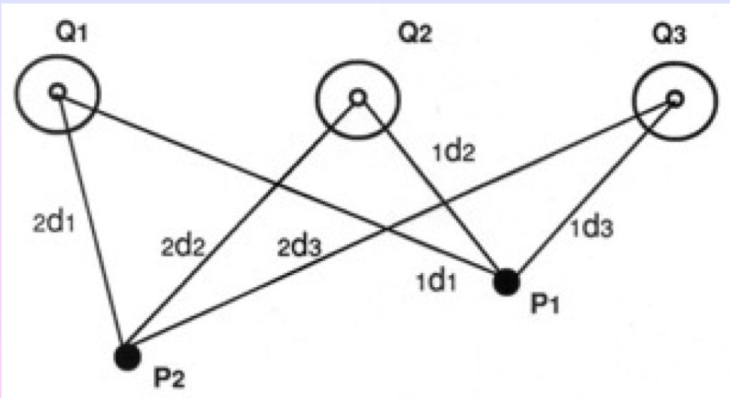


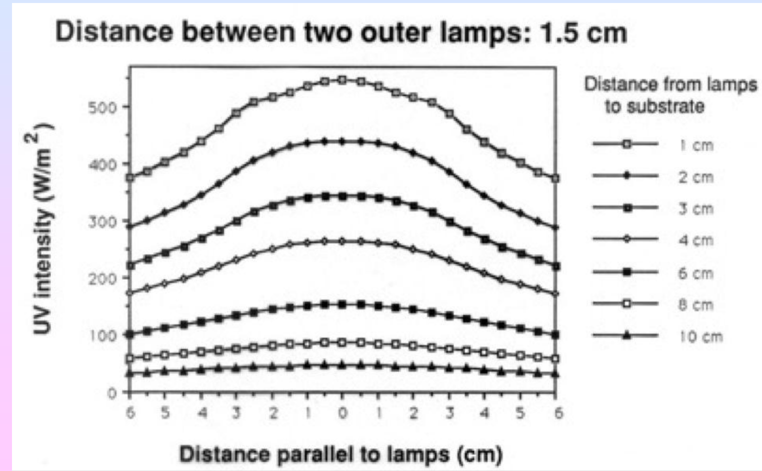
Large area excimer lamp system

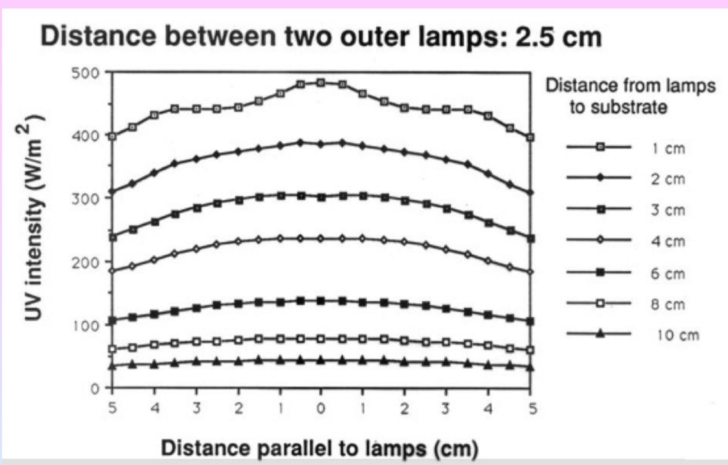


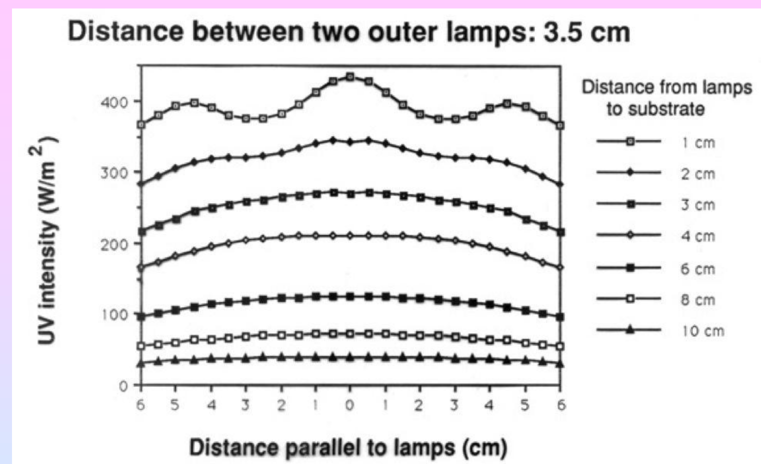


Uniformity modelling of three lamp system

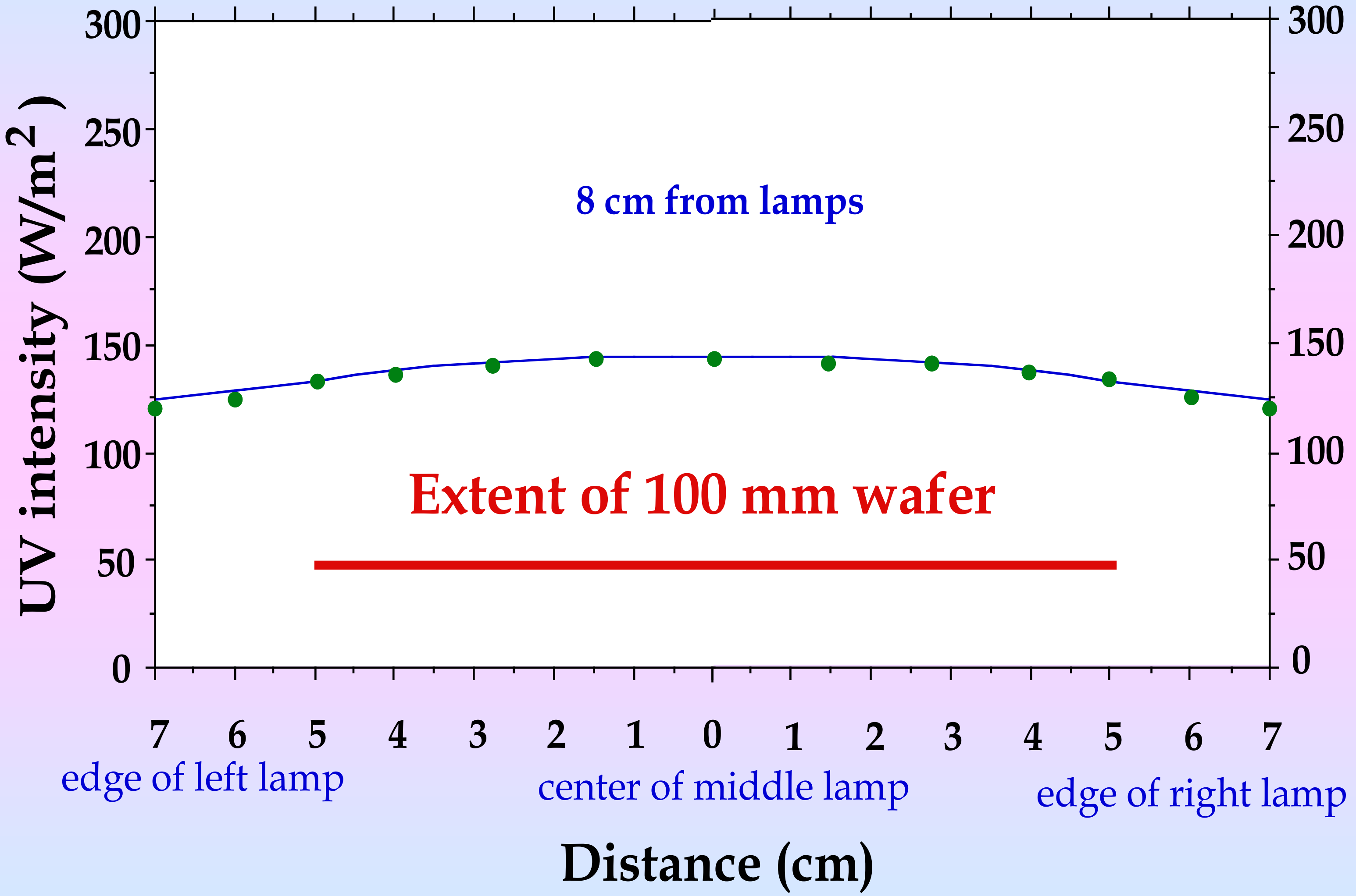








UV intensity profile of three lamp system



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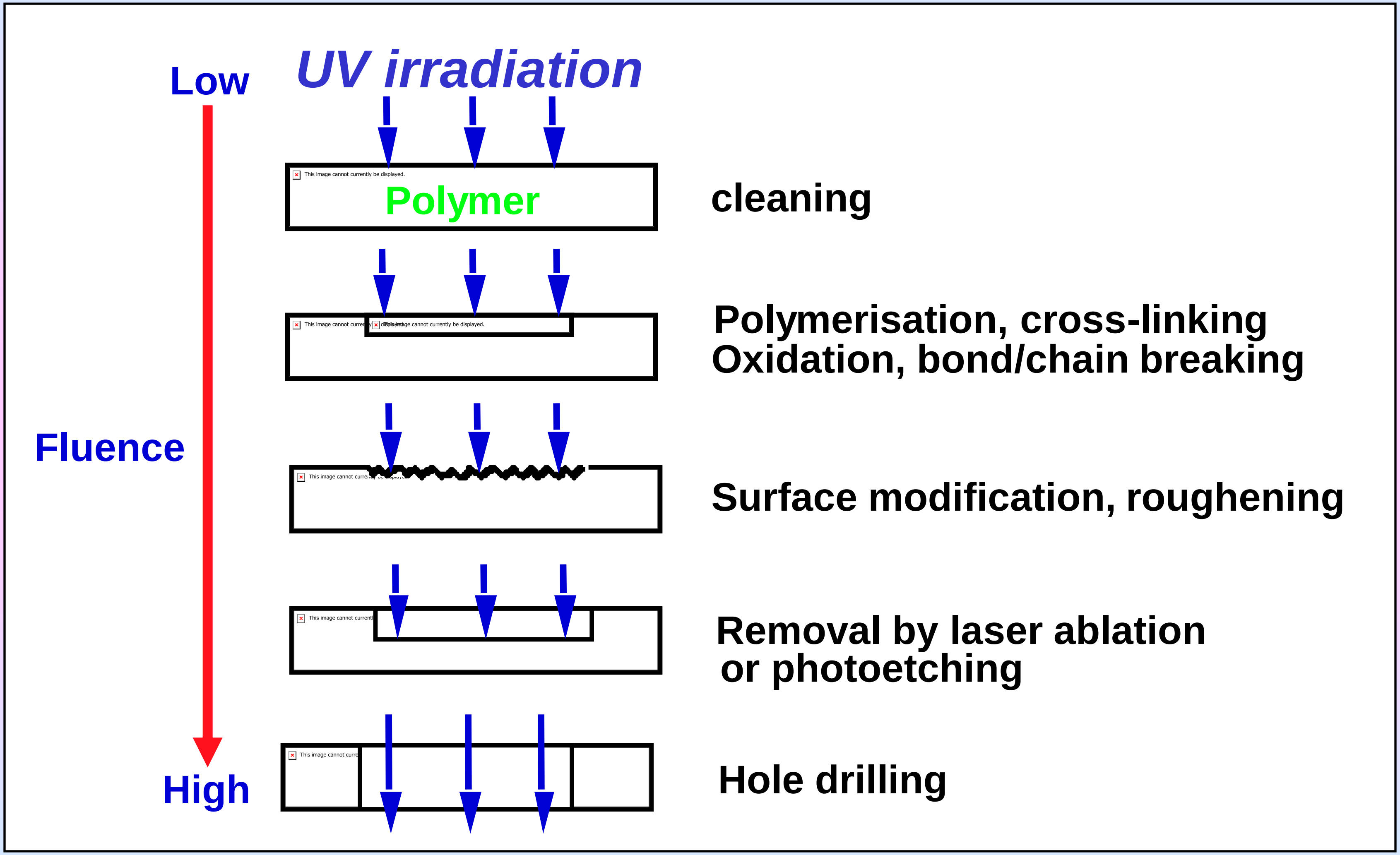
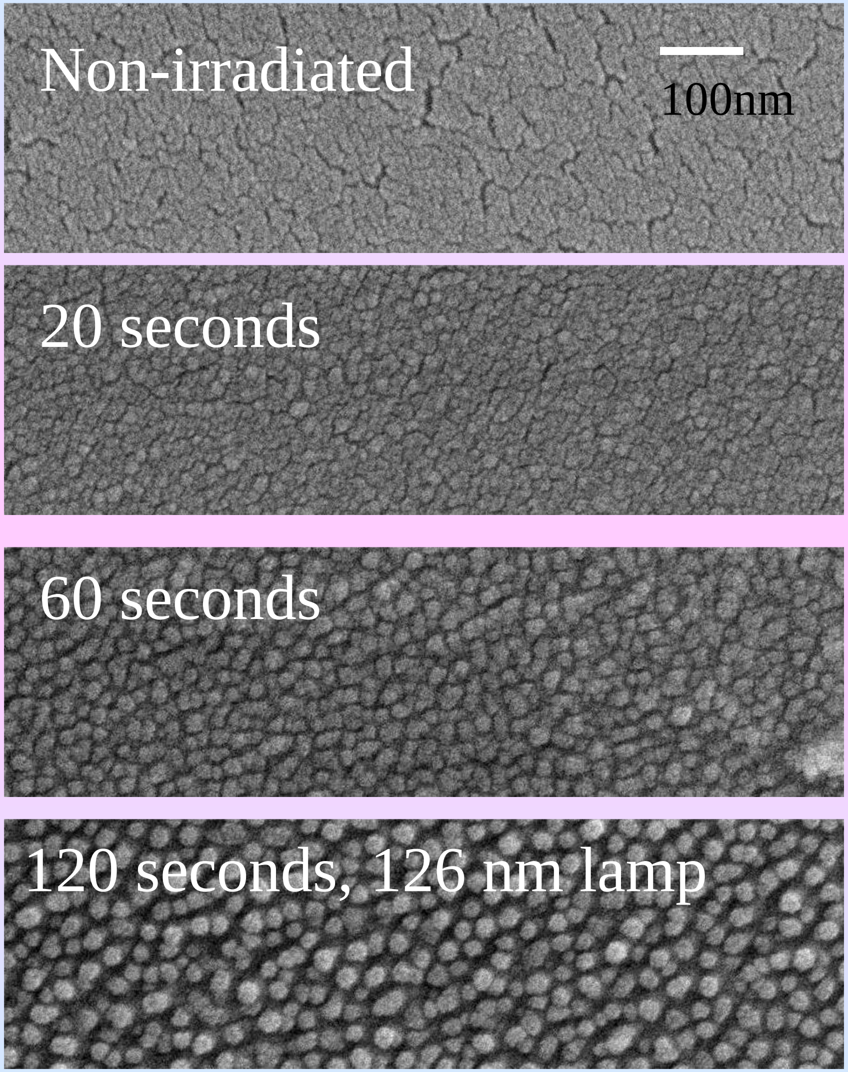
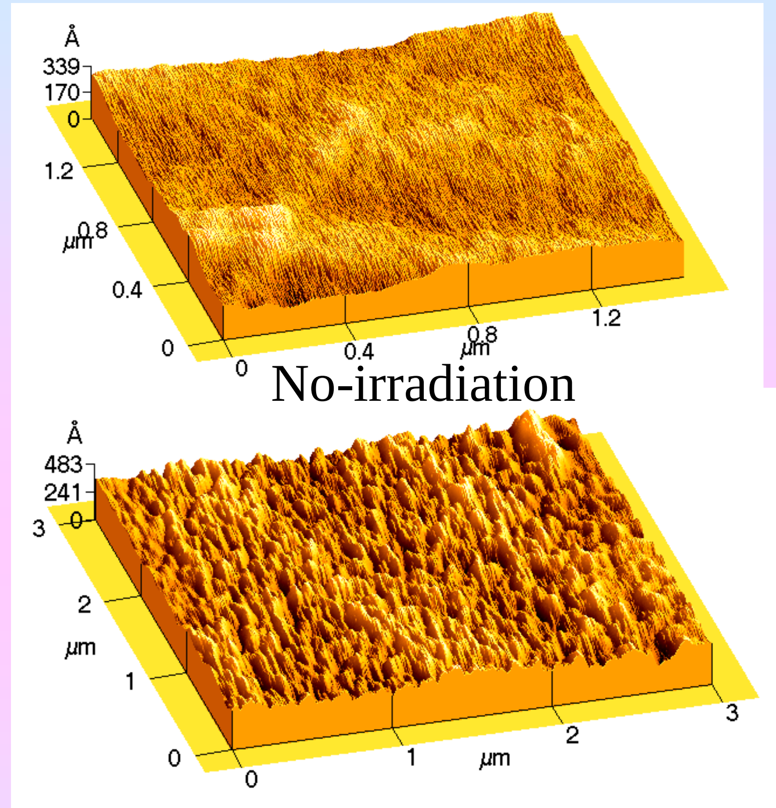
Treatment of Polymer Surfaces



VUV Surface Modification of Polymide: 126nm



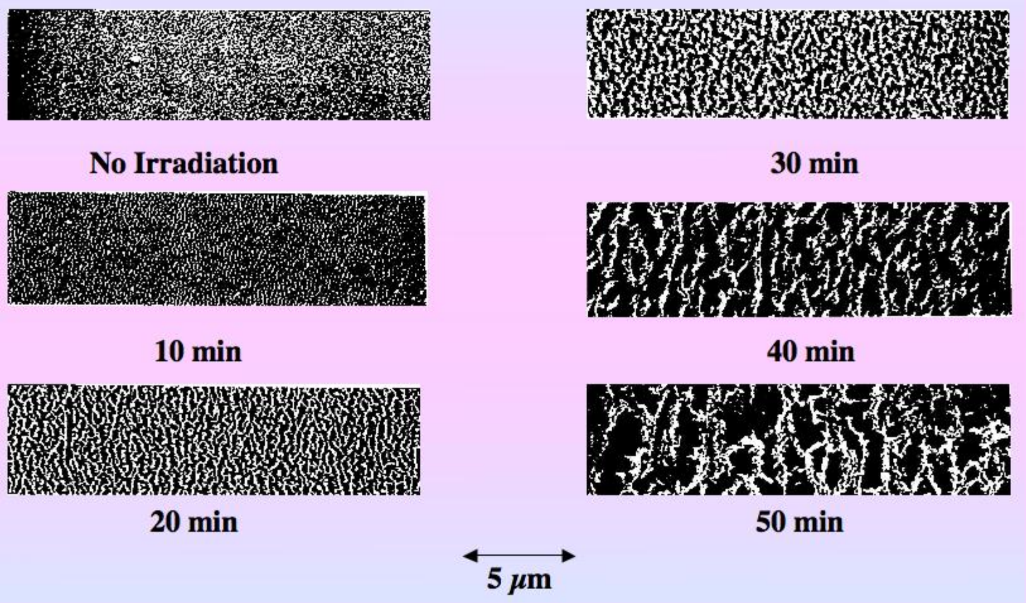


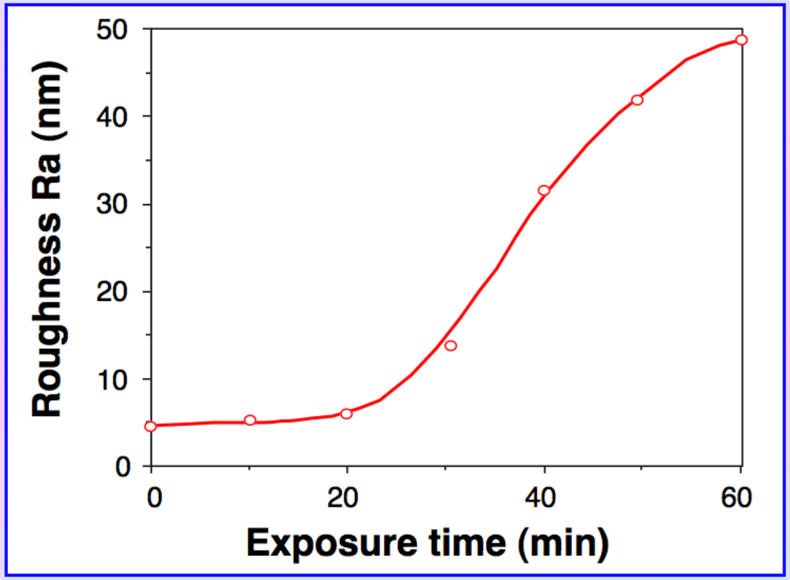
120 seconds, 126 nm lamp

XPS results show photo-dissociation of imide groups in Polyimide during 126 nm VUV irradiation

UV Surface modification of PET

Surface changes of PET irradiated for different times with a 222nm excimer lamp





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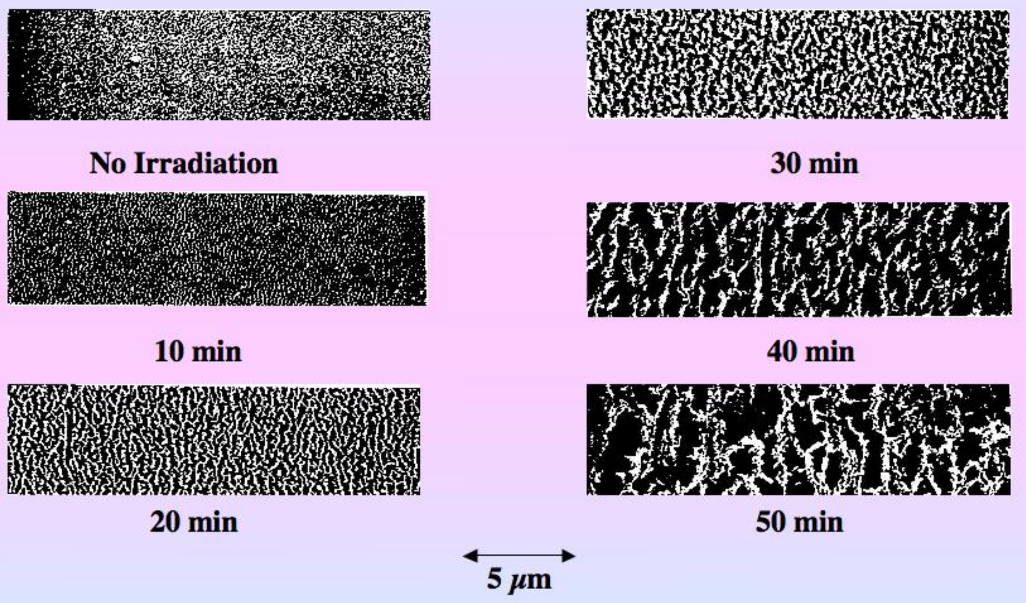
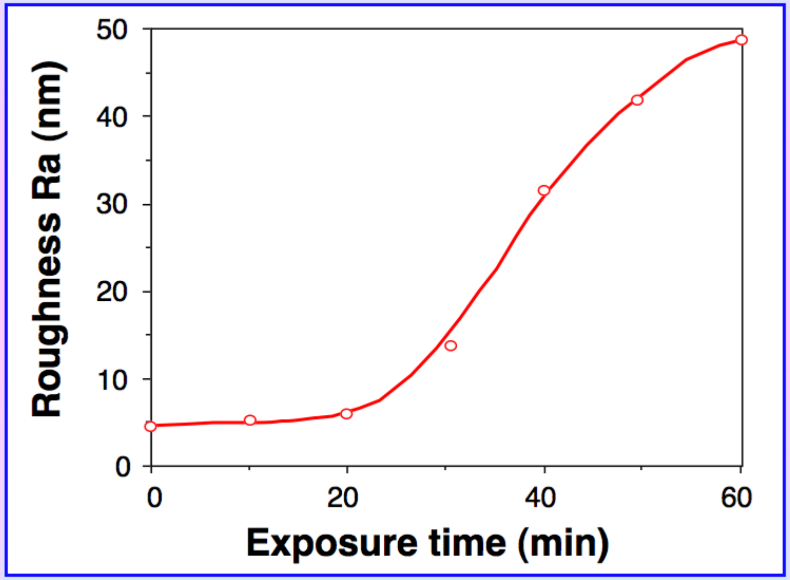
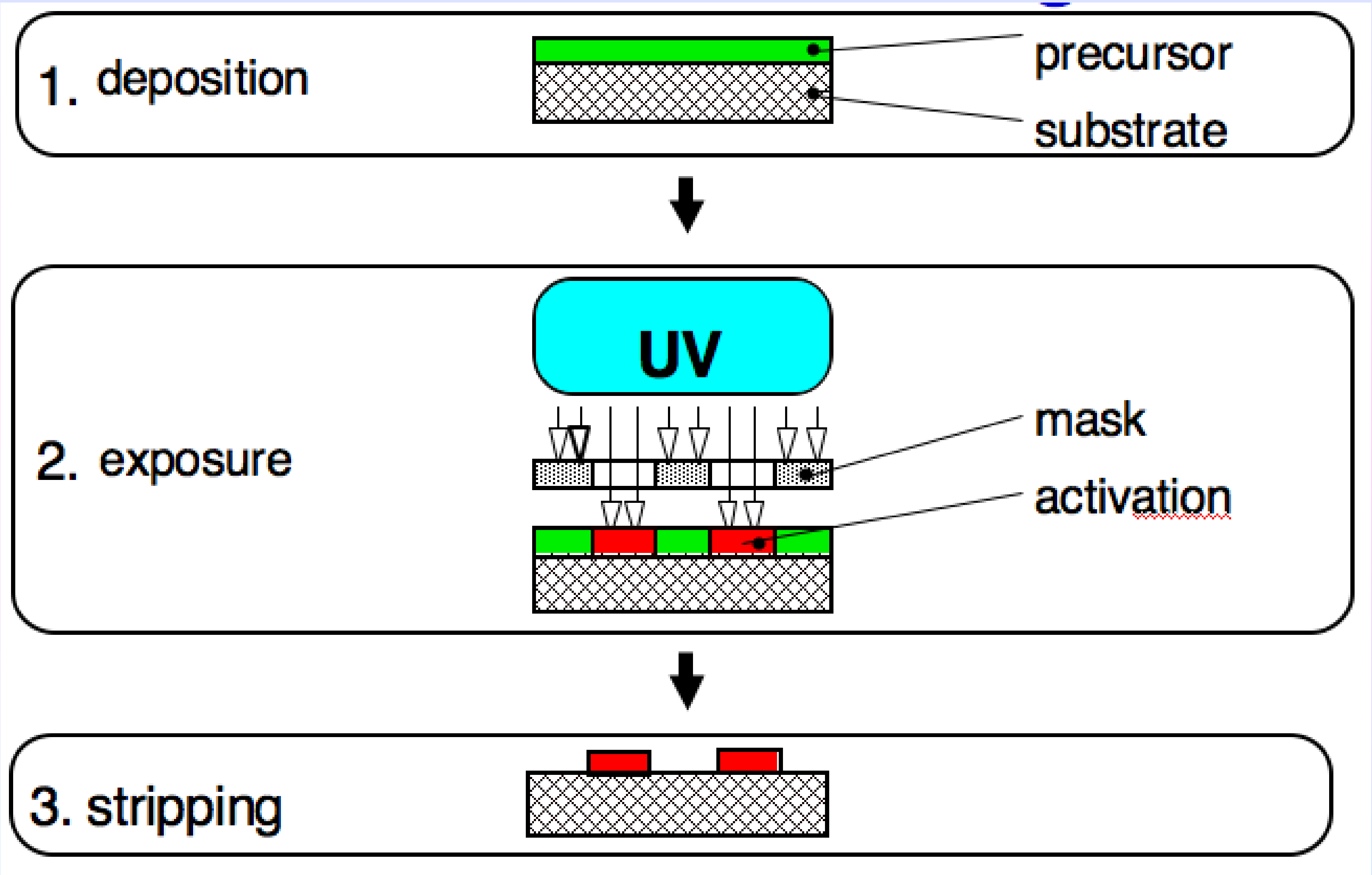


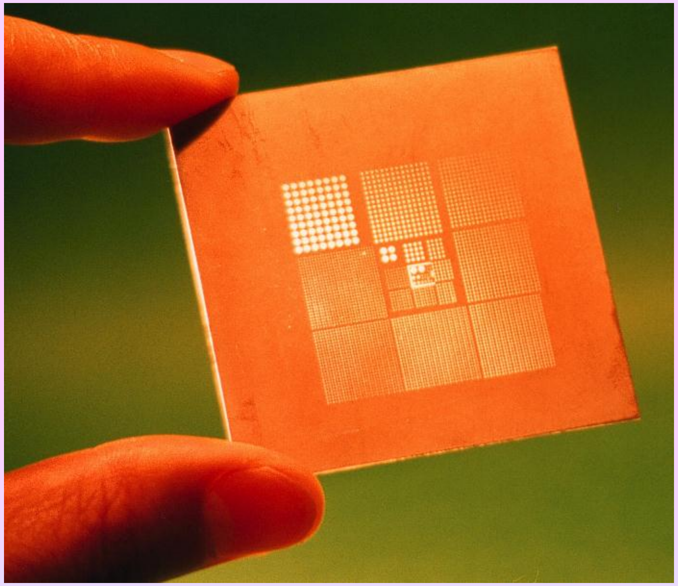


……….can be used to promote surface adhesion

Patterned Treatment of Polymer Surfaces



Copper structures on aluminium nitride



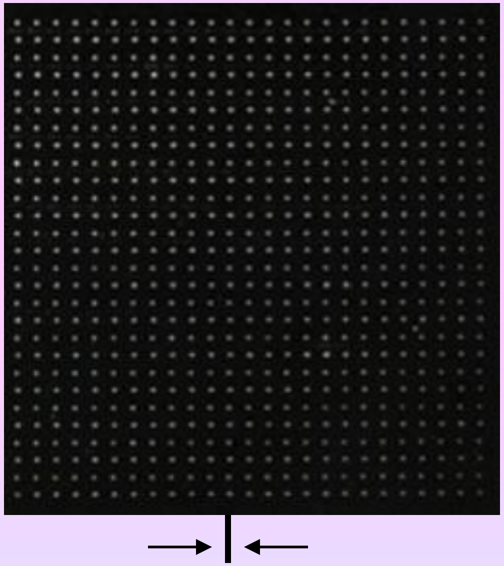
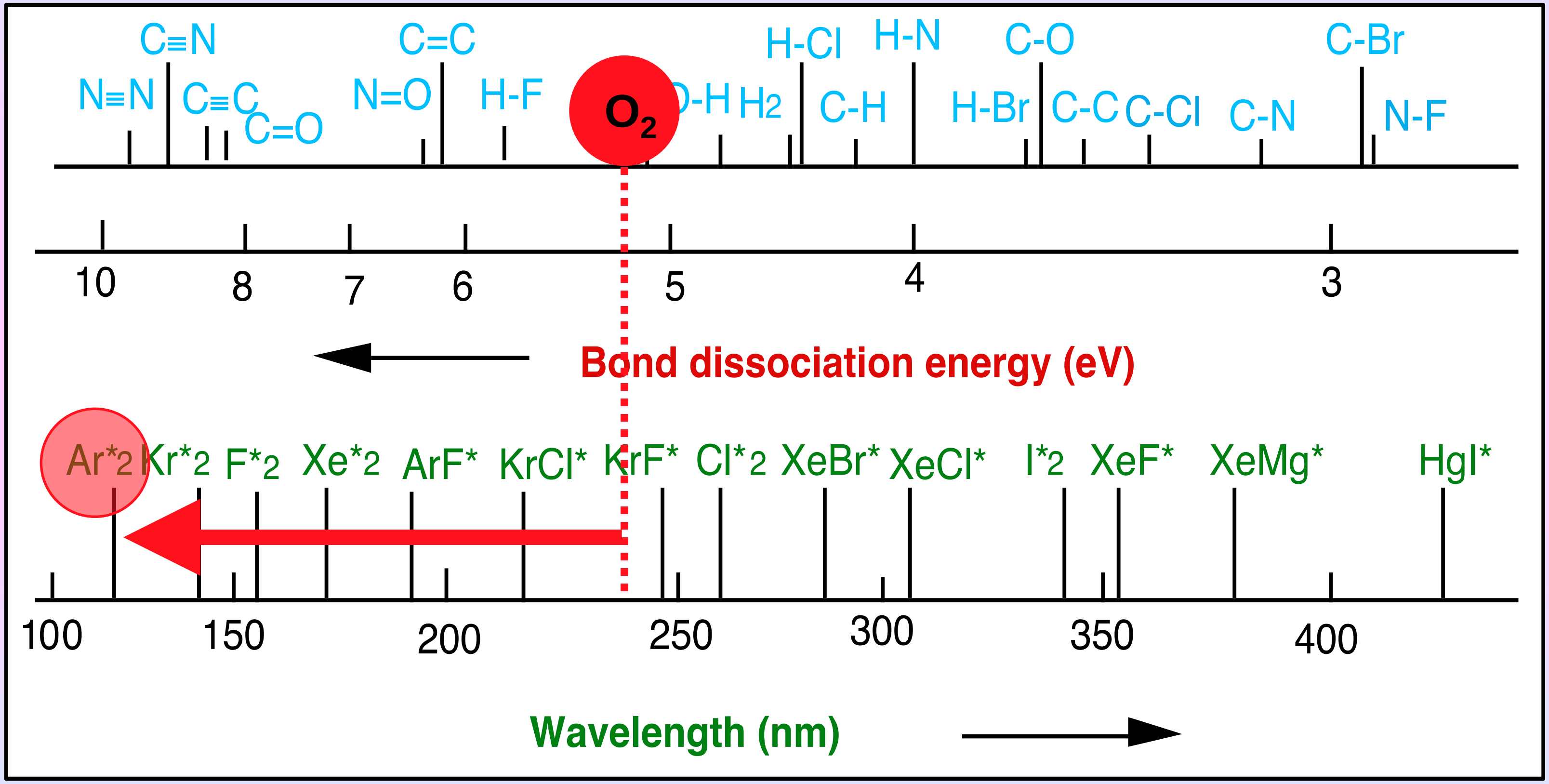
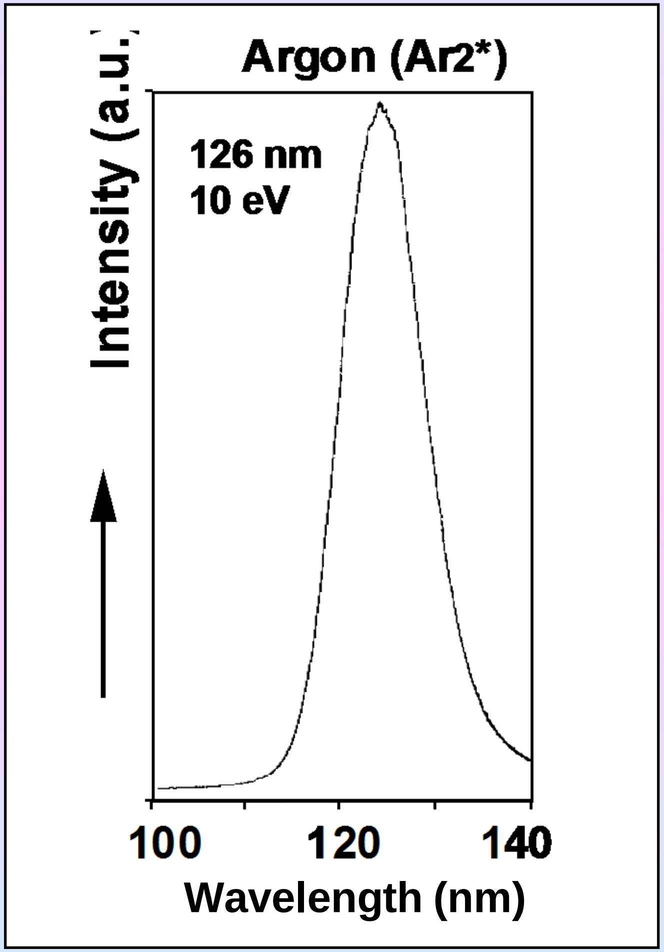


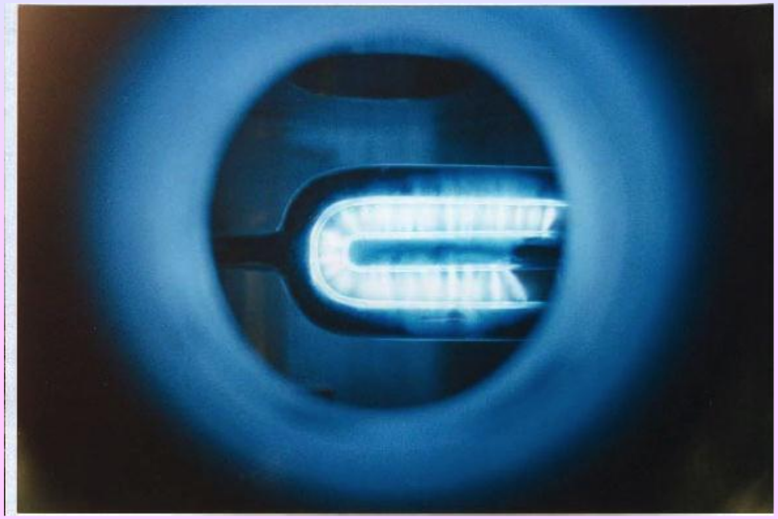
Photo-oxidation of Silicon: Si + $h\nu$ + O_2

Bond Dissociation Energy of Covalent Bonds and Wavelengths of Excimer UV Radiation



Emission spectrum of the second excimer continua of Ar_2^* rare gas dimer



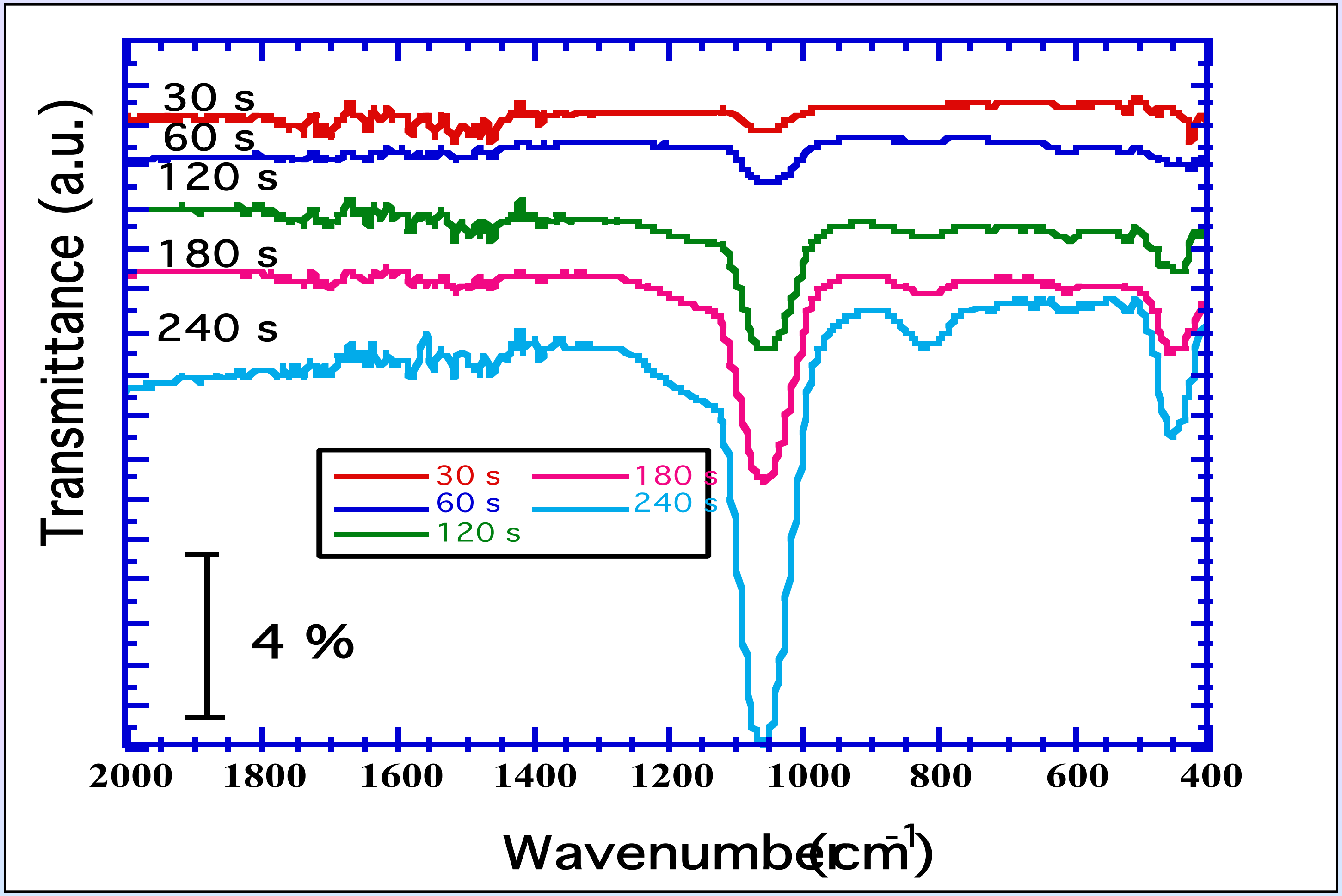


110.6 nm < λ < 134.2 nm

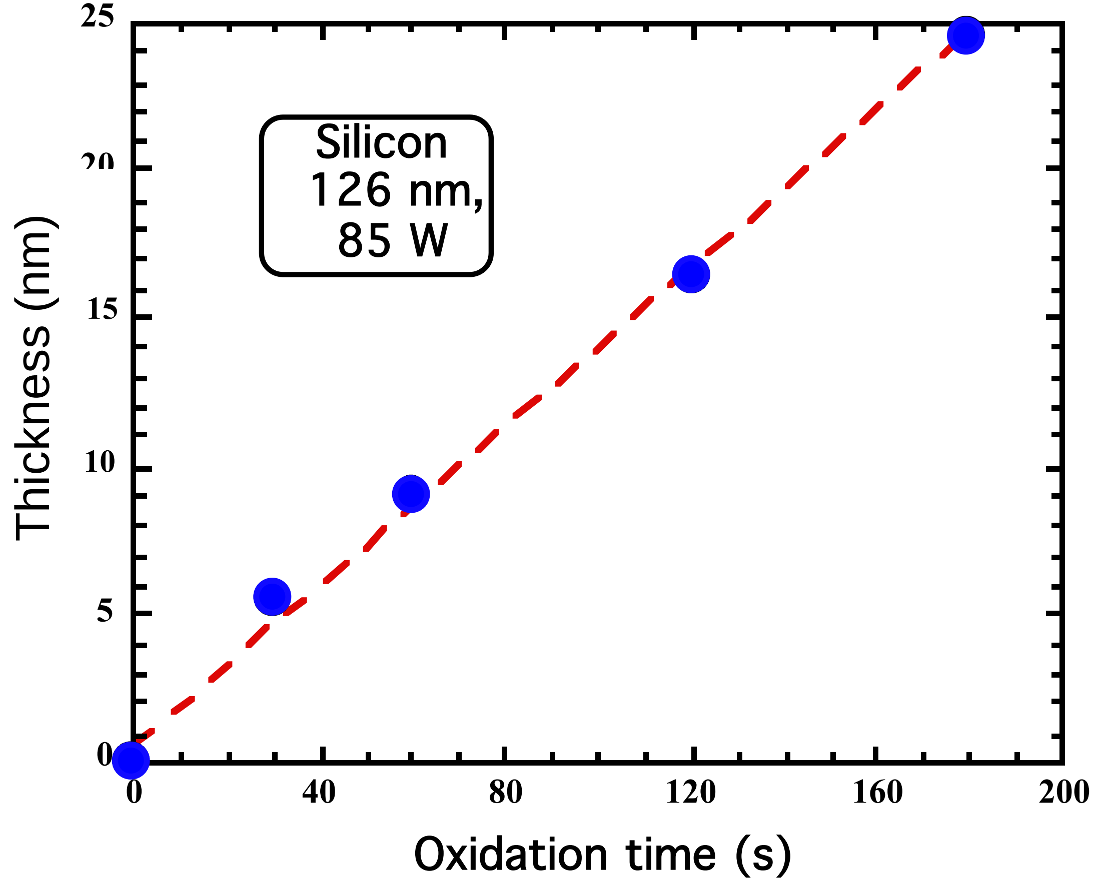
O_2 ($^3{}_g{}^-$) + hν → $O(^3P)$ + $O(^1S)$ ΔH_o=897.80 kJ/mol

So the 126 nm light should promote the most rapid Si oxidation since it creates very highly energetic excited $O(^1S)$ species

FTIR spectra of SiO_2 grown by 126nm excimer lamp at room temperature

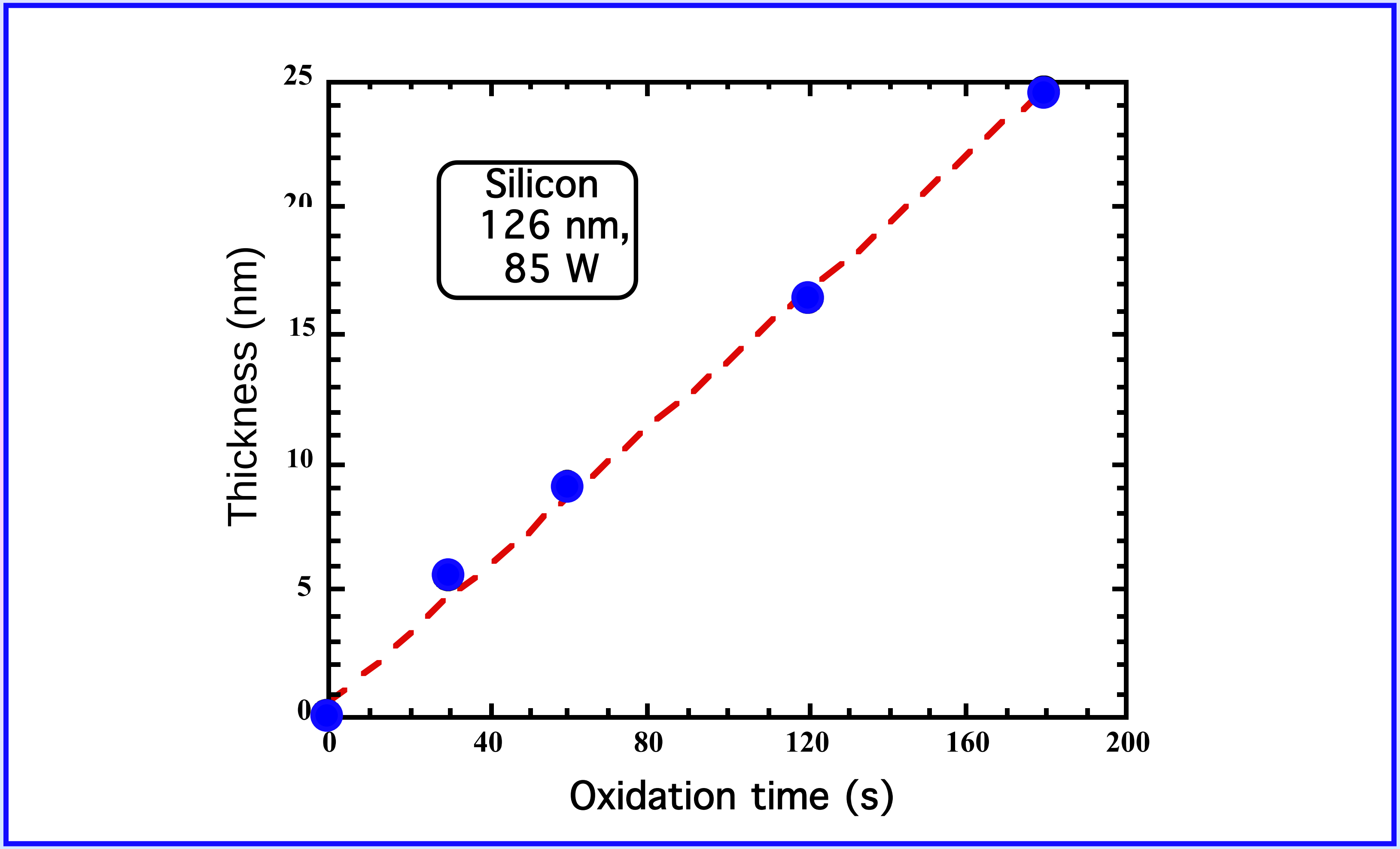


Growth of SiO_2 with 126 nm excimer radiation:



Growth of SiO_2 with 126 nm excimer radiation:

Room Temperature !



126nm Oxidation: Summary

Successful room temperature oxidation of Si using 126nm radiation

XPS and FTIR confirm high quality and stoichiometric SiO_2 formed.

Leakage current densities as low as 5 $x10^{-8}$ A/cm^2 at an applied electric field of 1 MV/cm.

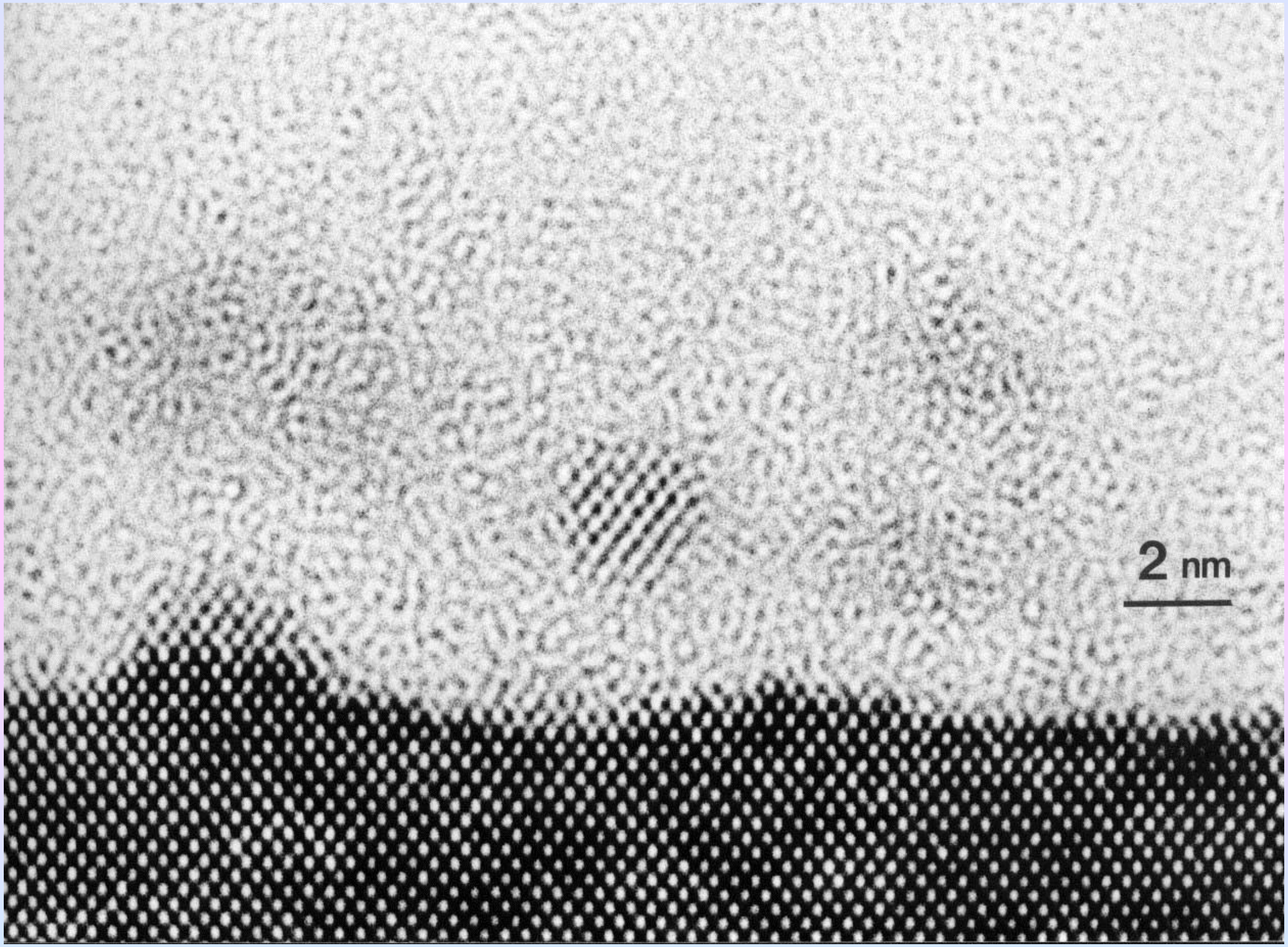
Significant oxidation rates, as high as 8 nm/min achieved.

Thicknesses up to 24 nm readily obtained with no growth saturation.

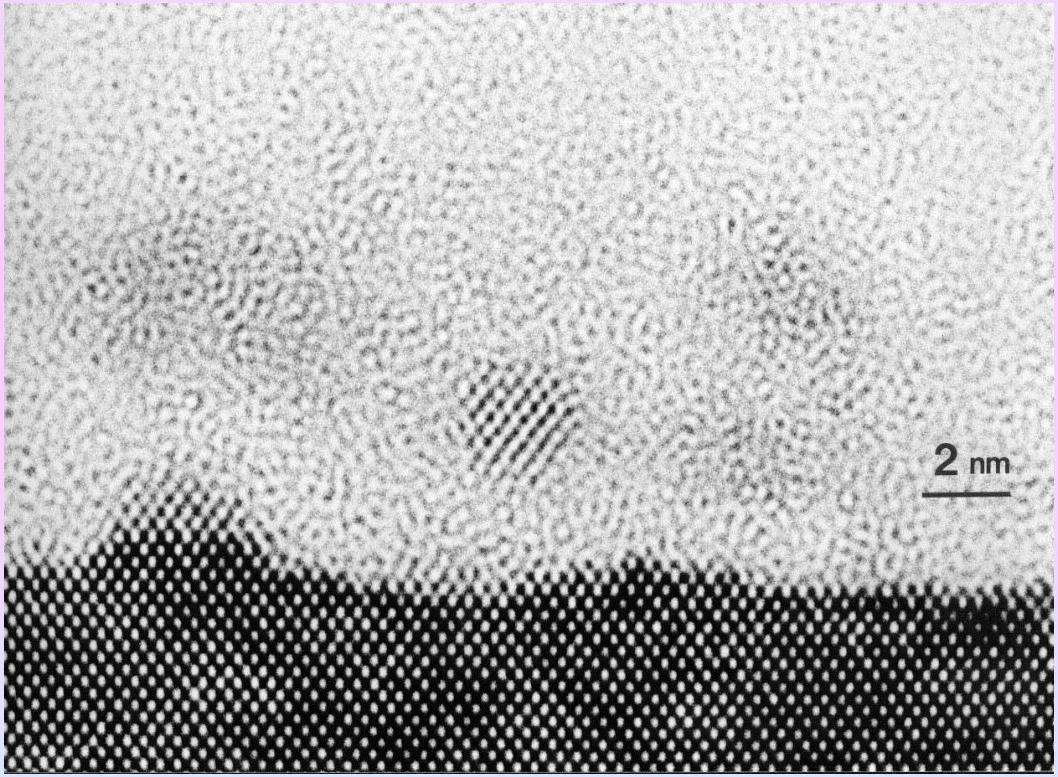
Rapid oxidation related to creation of aggressive O_{1S} oxidant.

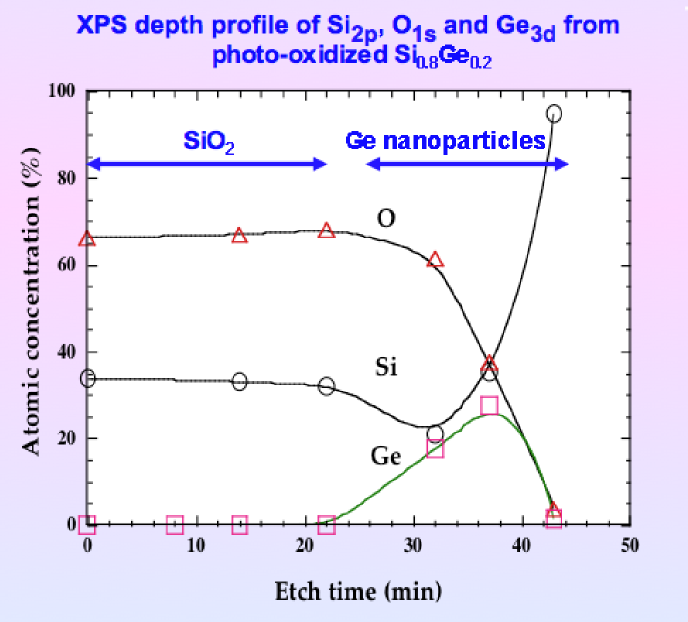
Photo-oxidation of Silicon-Germanium

High-resolution XTEM image of UV Oxidised SiGe

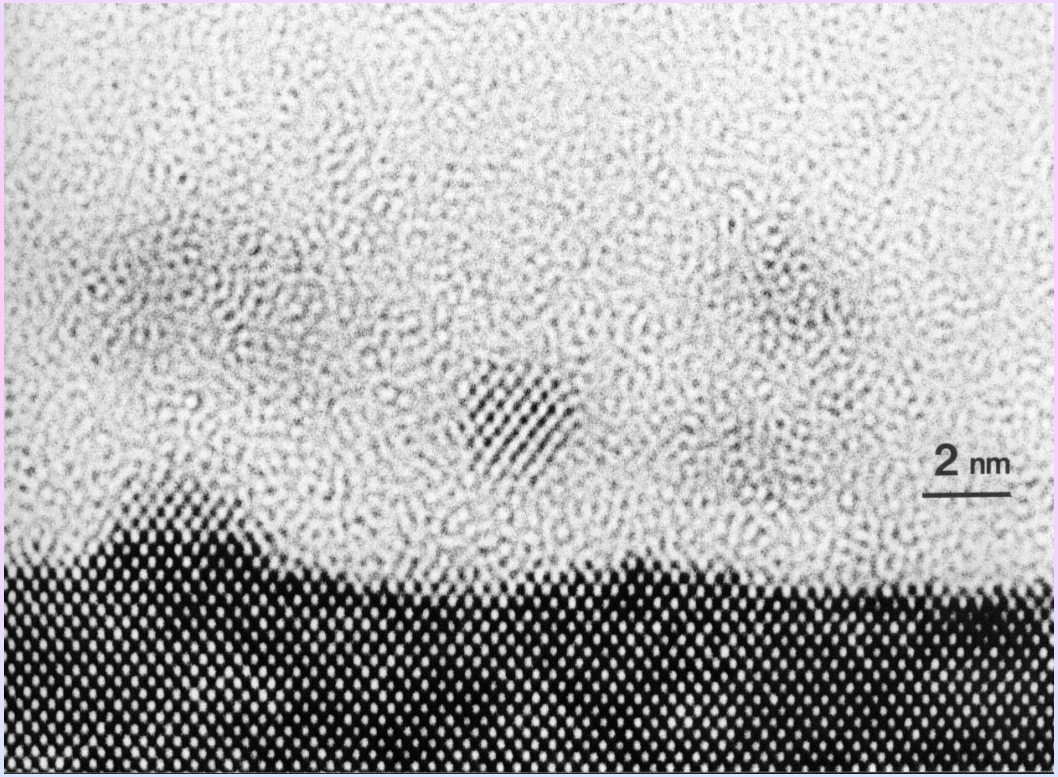


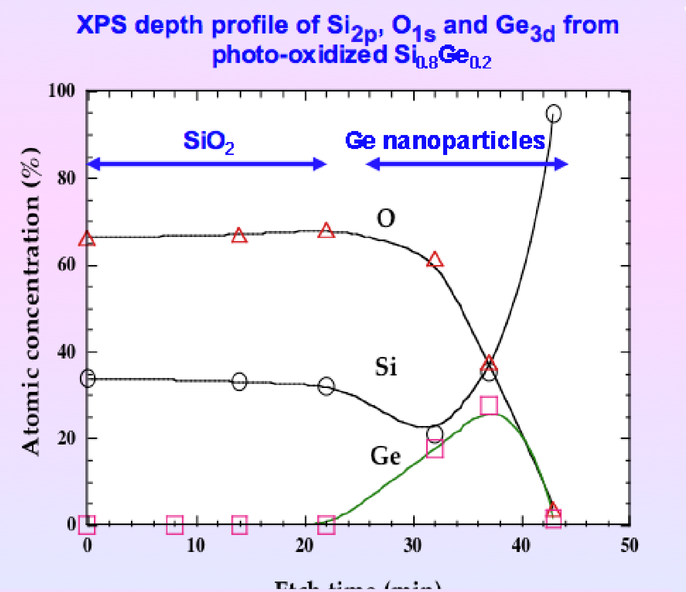
High-resolution XTEM image of UV Oxidised SiGe

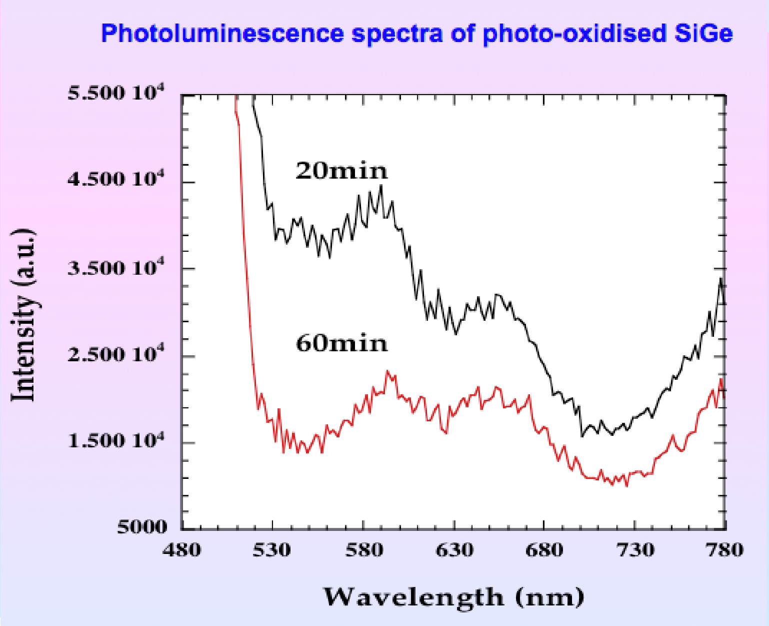




High-resolution XTEM image of UV Oxidised SiGe







Outline of Talk

1. Principles & properties of UV Excimer Lamps

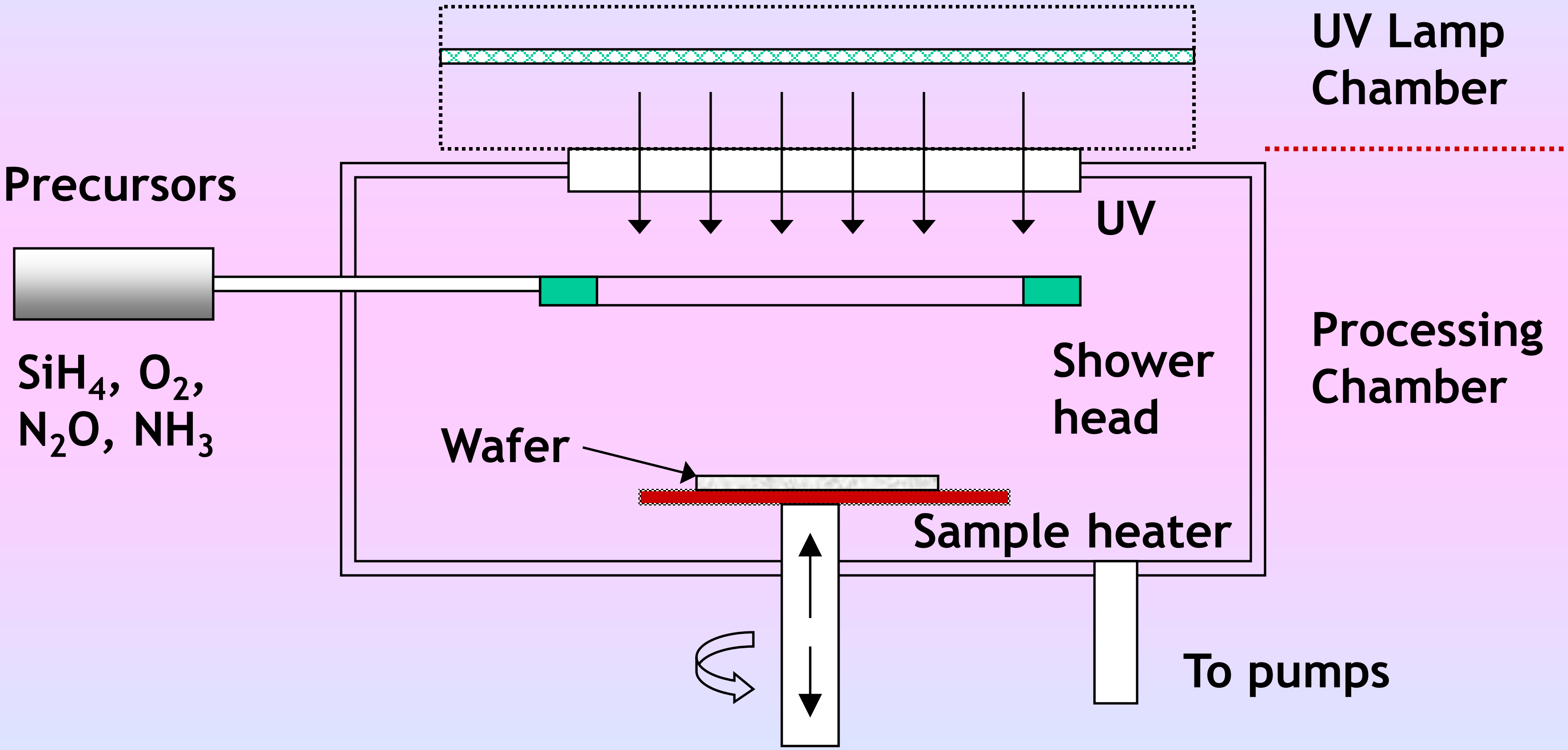
2. Development of UV deposition system

3. **Potential Applications:**

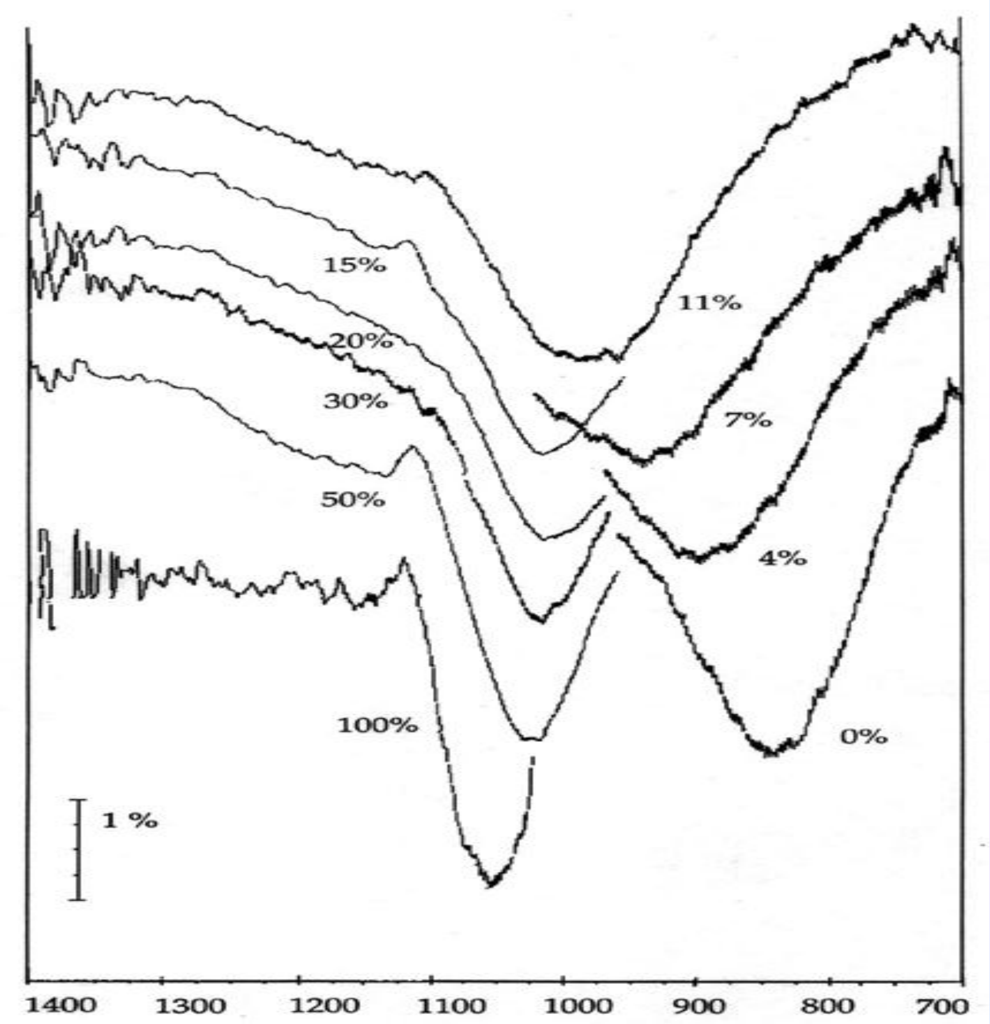
   Surface engineering
   Oxide, metal deposition
   Interface engineering
   Nanoparticle deposition & doping

Photo DEPOSITION of Dielectrics

Photo-CVD Apparatus

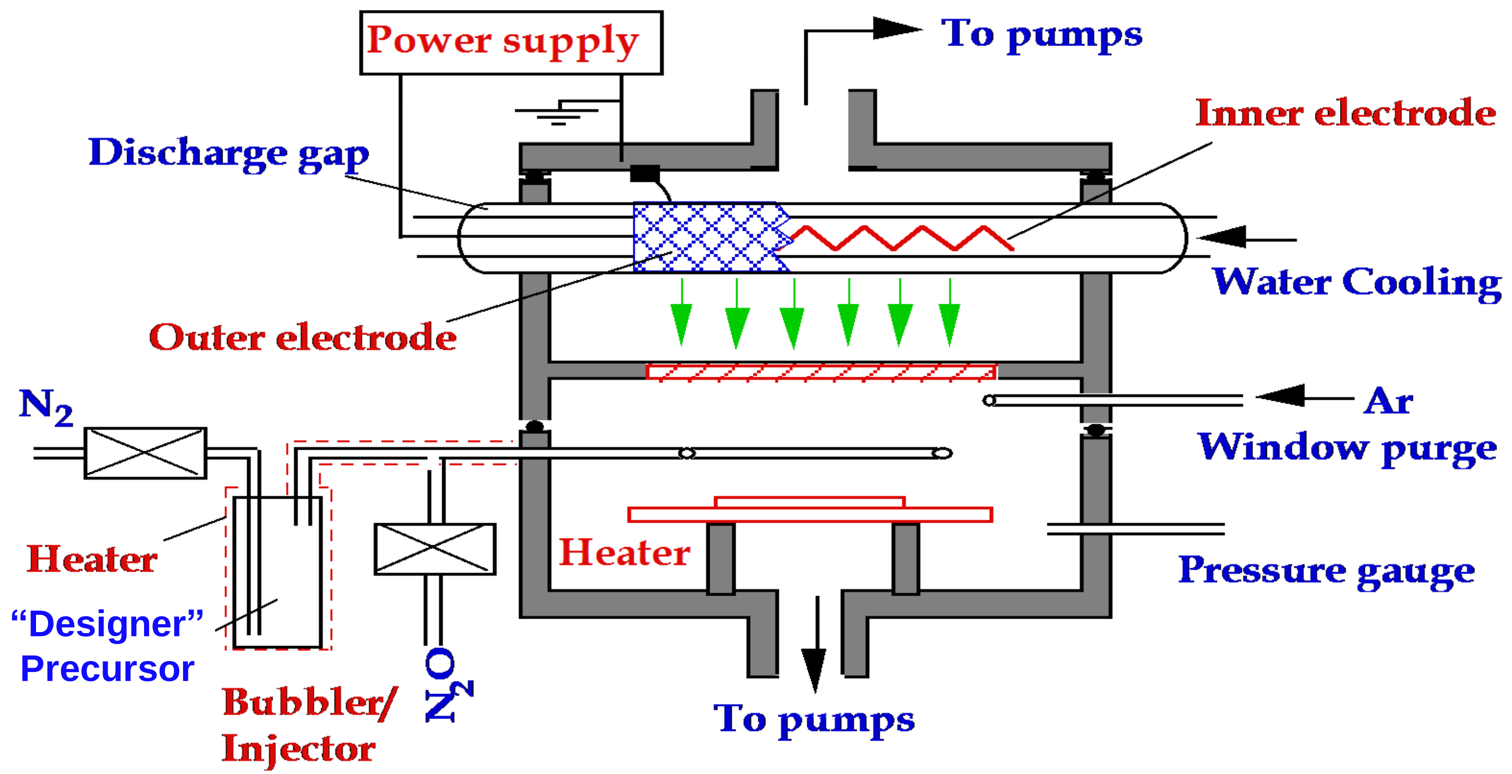


Deposition of Si oxide, oxynitride, and nitride using SiH_4 with various N_2O/NH_3 precursor ratios



Metal Oxide Deposition:

Photo-CVD reactor incorporating bubbler/digital liquid injection & "designer" precursors



Excimer lamp deposition of metal oxides using UV-Injection Liquid Source (UVILS):

TiO_2

Ta_2O_5

HfO_2

Excimer lamp deposition of metal oxides using UV-Injection Liquid Source (UVILS):

TiO_2

Ta_2O_5

HfO_2

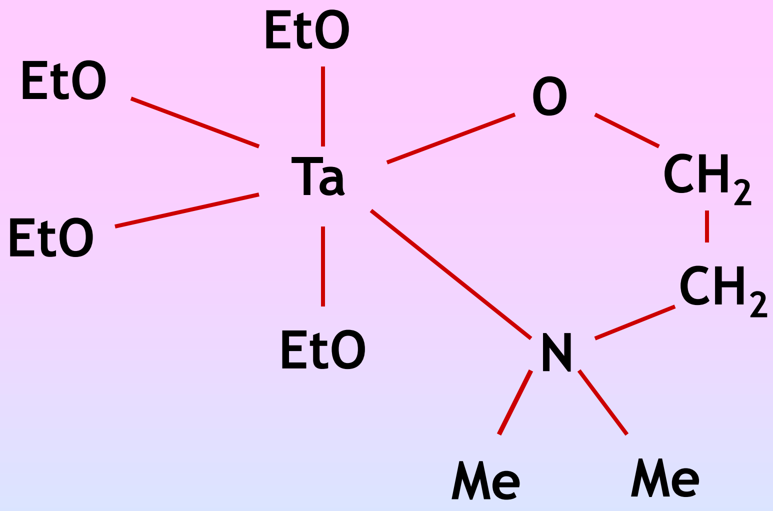
Tantalum Precursor

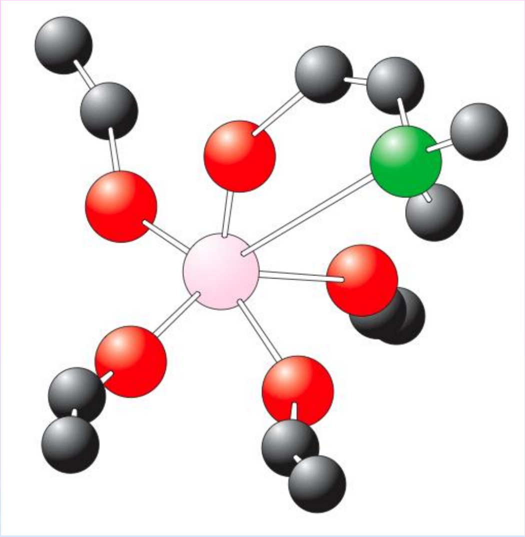
Tetra ethoxy (dimethyl amino ethoxy) tantalum

- Ta $(OEt)_4$ (O CH_2 CH_2 N Me_2)

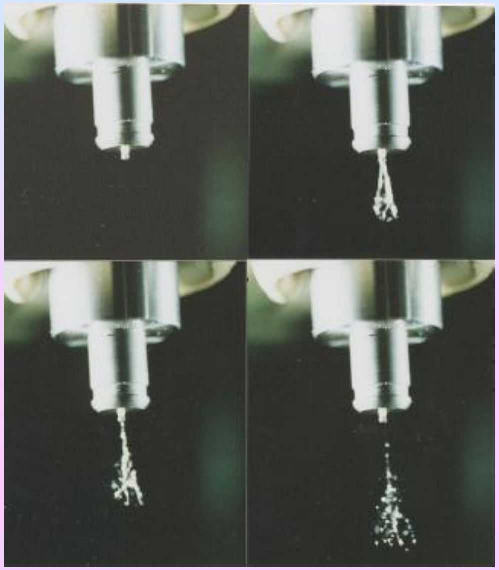
Et : CH_3 - CH_2

Me: CH_3



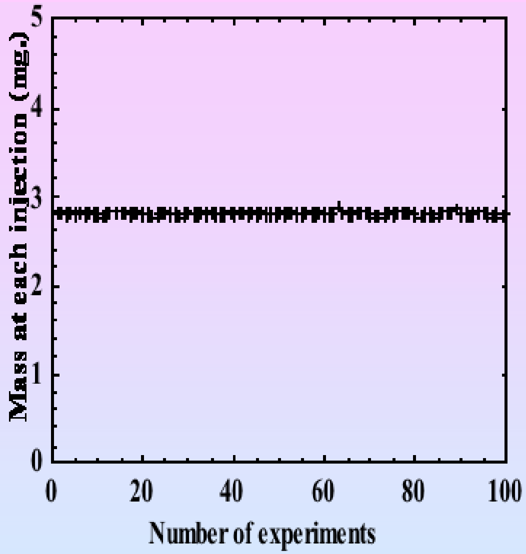


Precursor Injector



INJECTION OF PRESSURISED LIQUID BY A FAST MICRO ELECTRO VALVE

FLASH EVAPAORATION

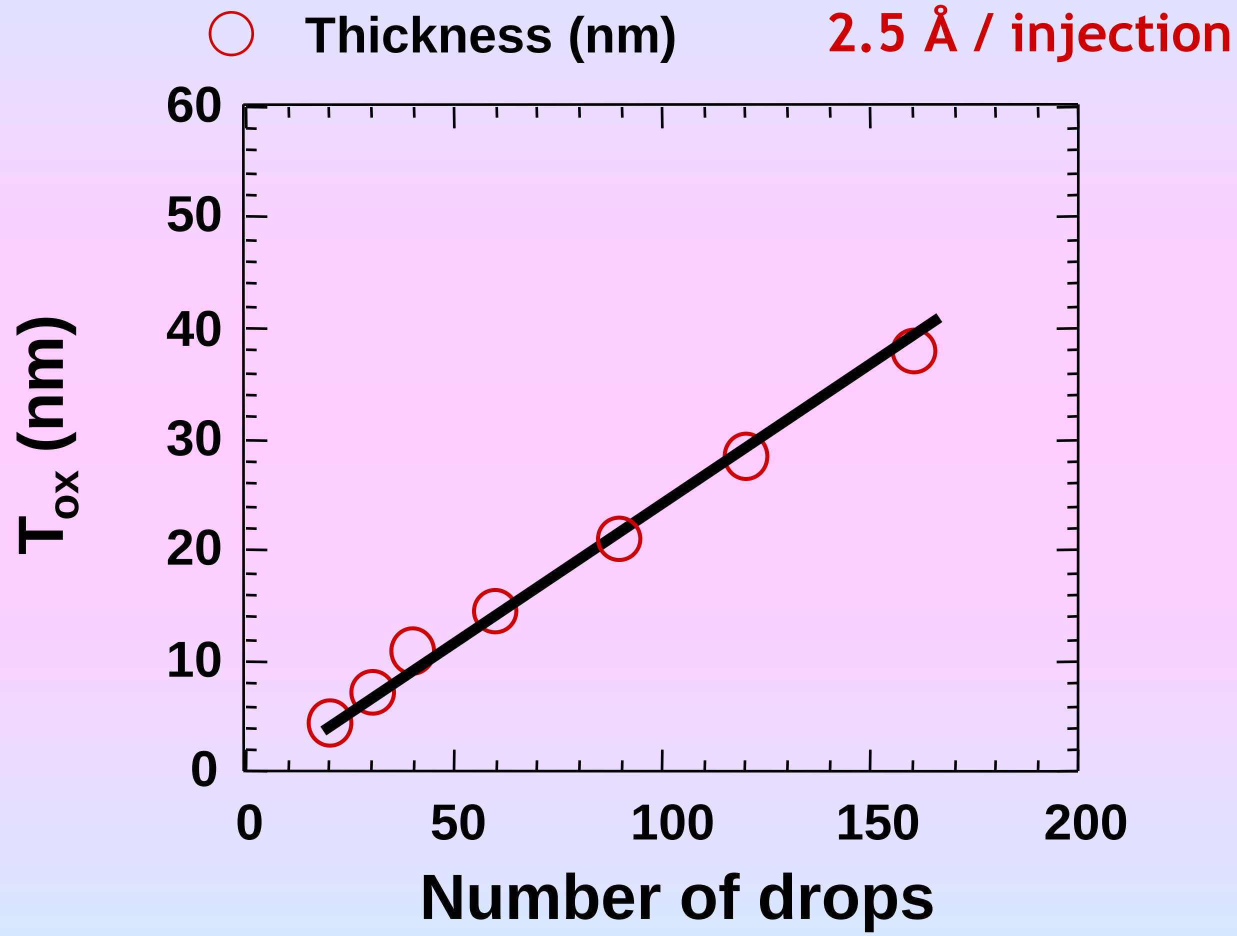


Precise Control of Mass of Precursor/solvent Introduced to Processing Chamber

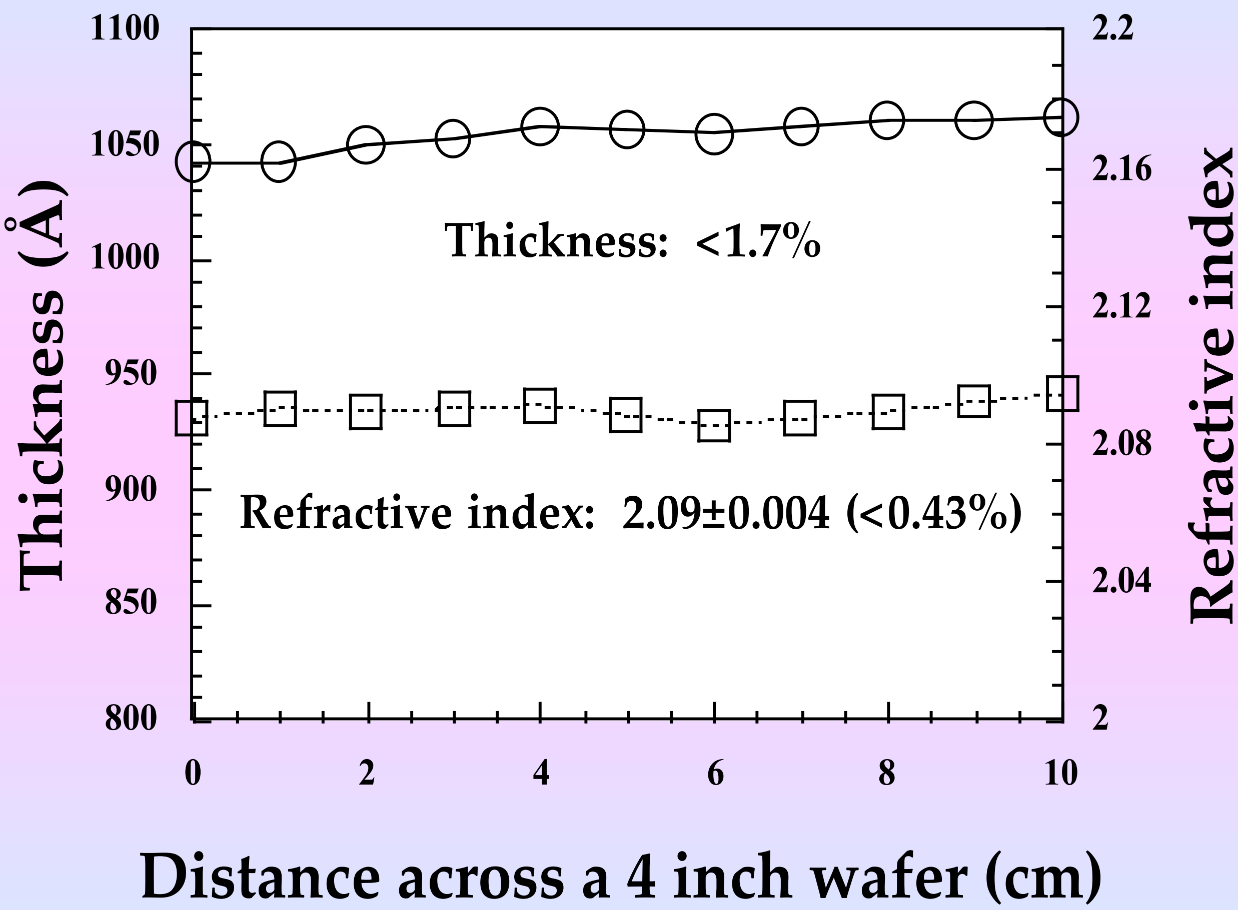
Flow Rate Fixed by F x Aperture time)

Film thickness fixed by no. of injections

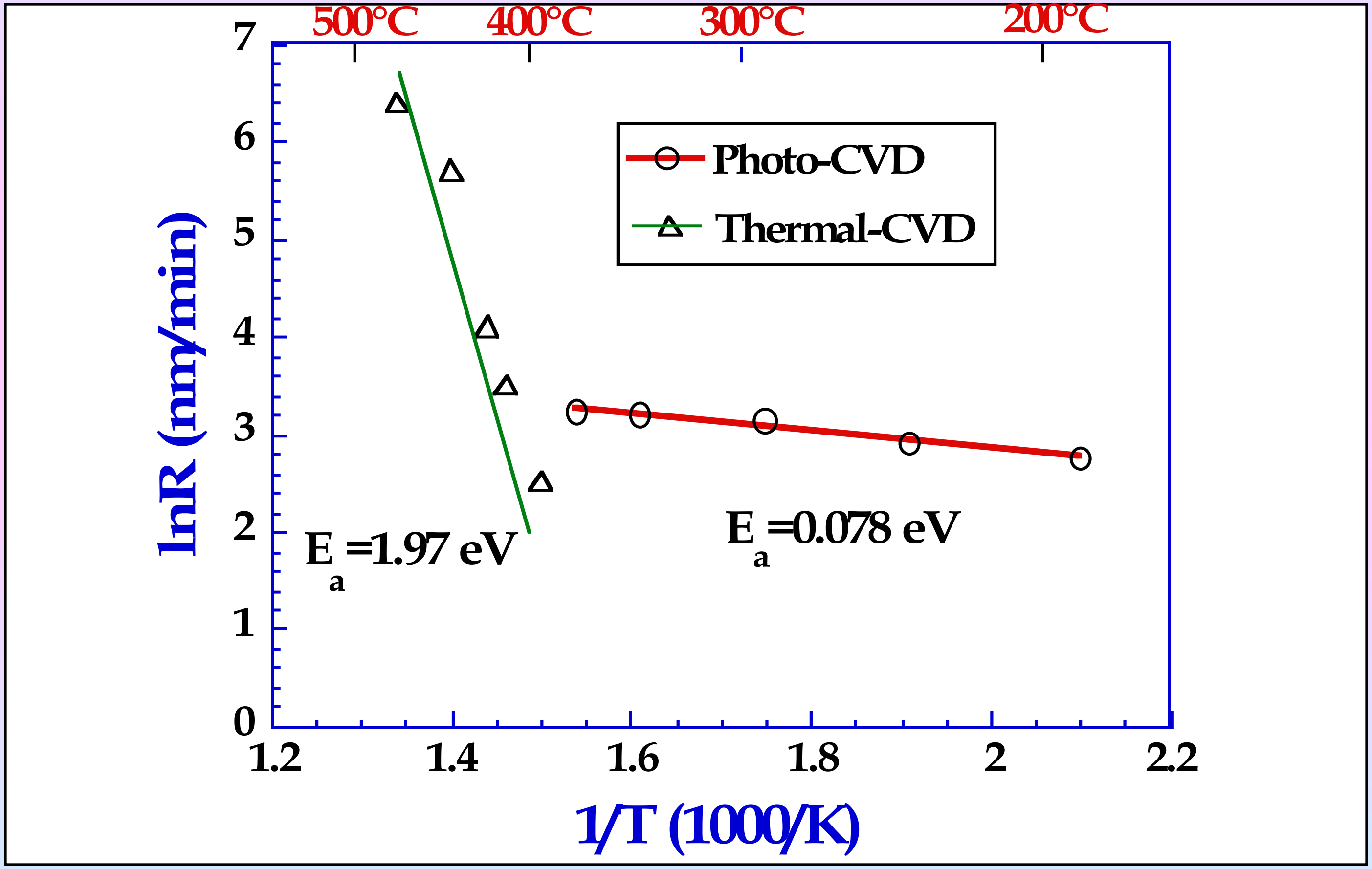
UVILS-CVD: Ta_2O_5



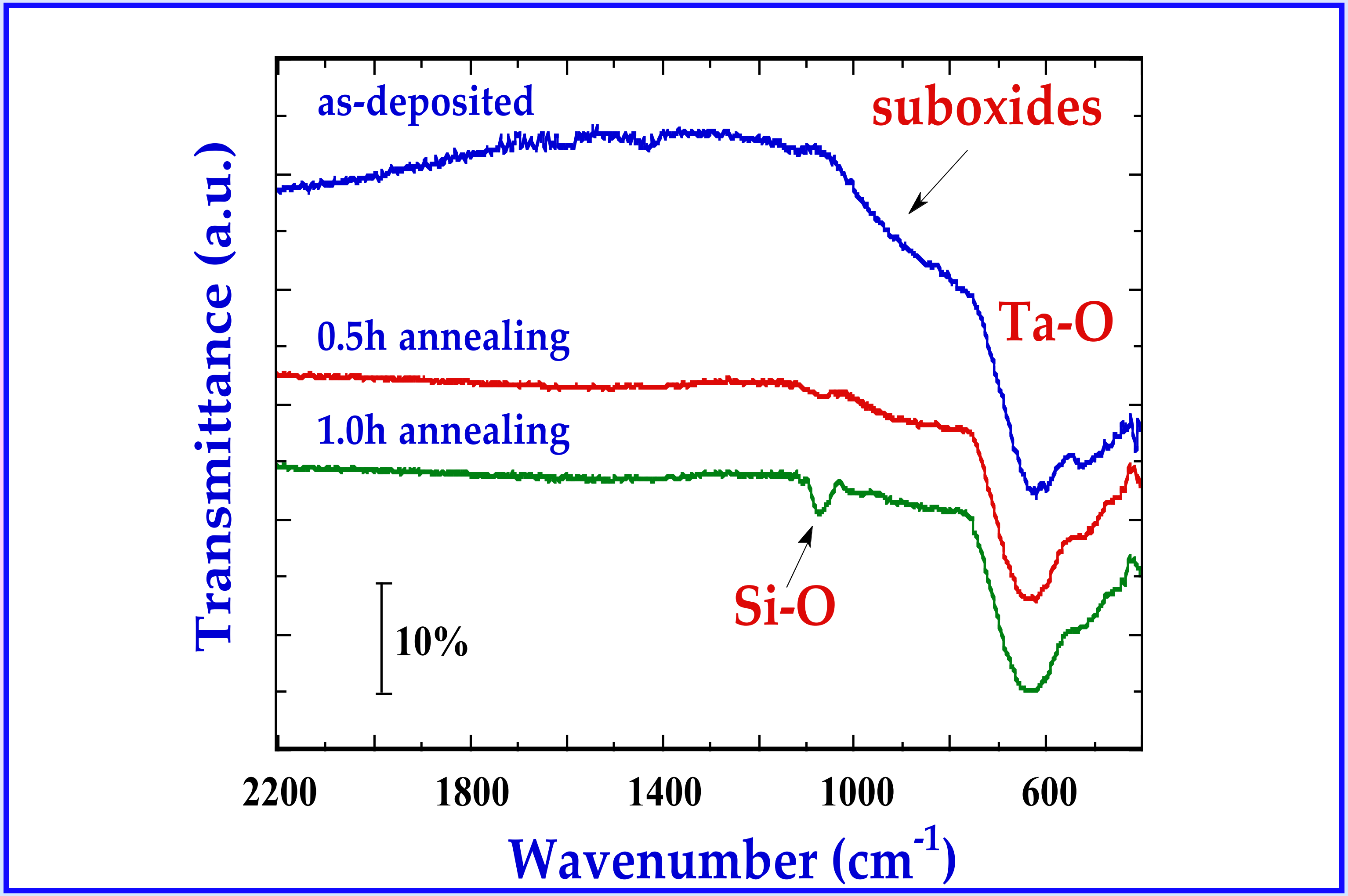
Uniformity of UV processed Ta_2O_5 films



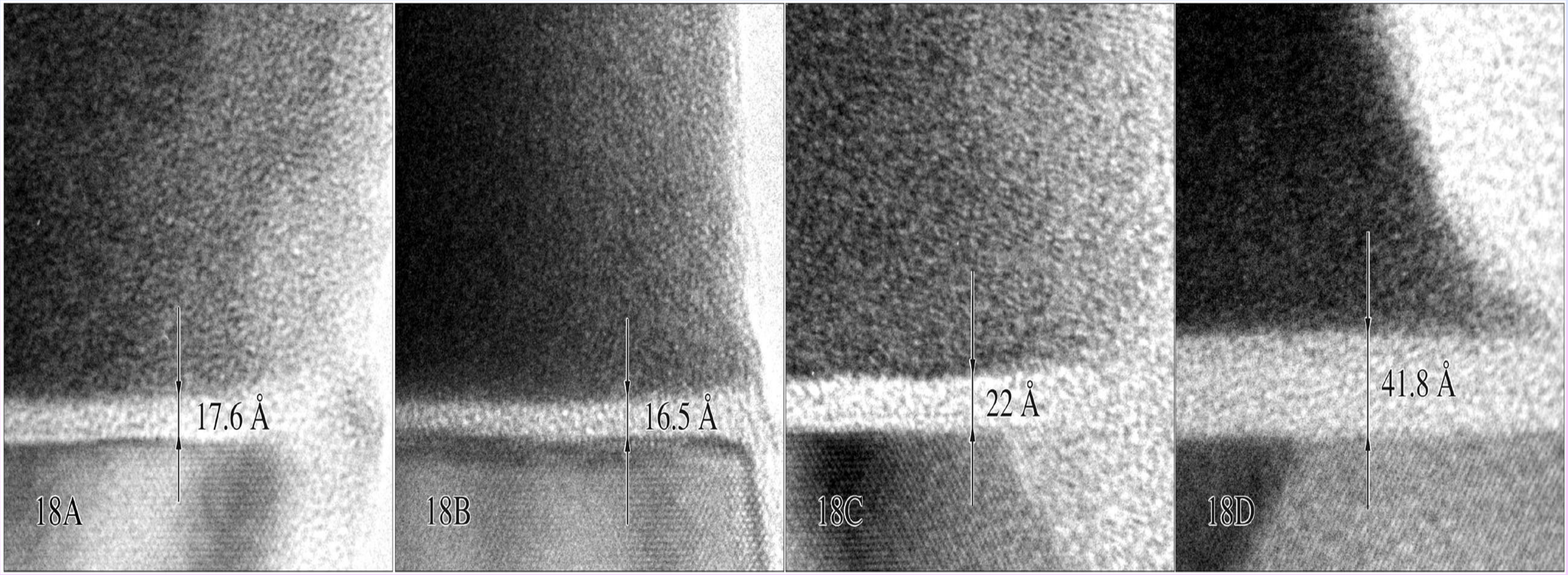
Growth rate of photo- and thermal- CVD of Ta_2O_5 films



FTIR spectra for for Ta_2O_5 films deposited by photo-CVD at 350° C and UV annealed at 400° C

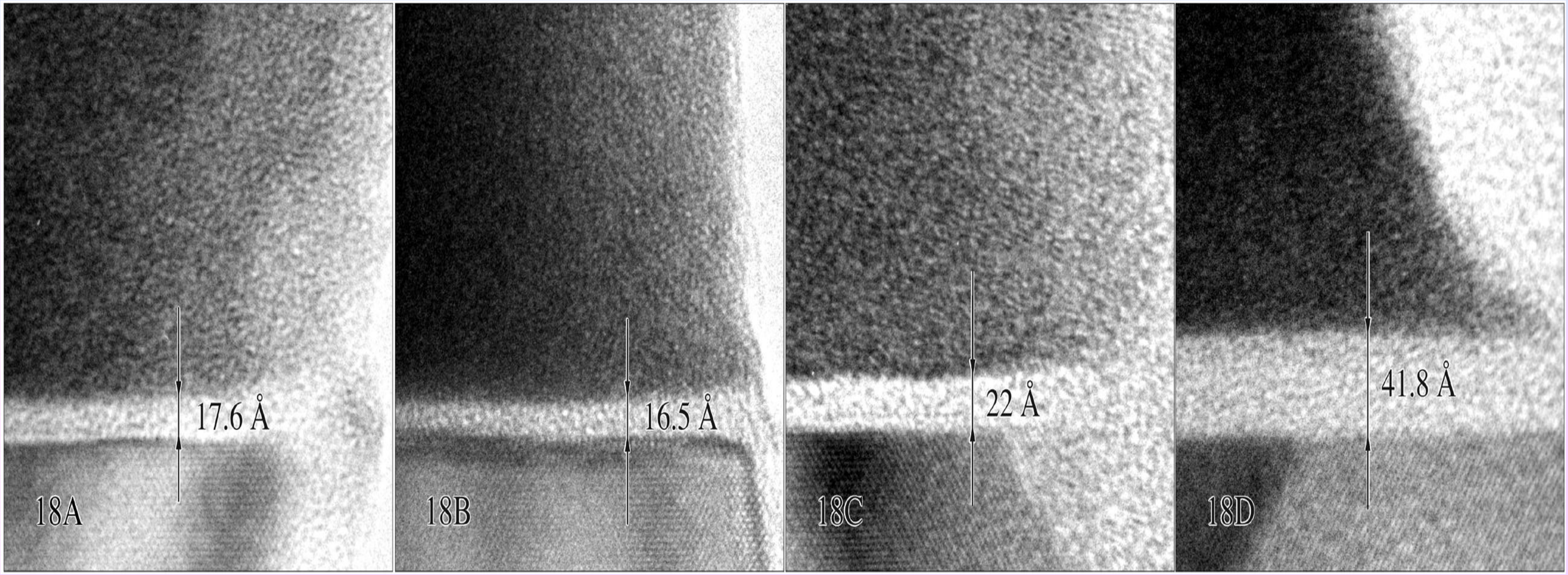


The SiO_2 interface layer: UV Annealing



As deposited **15 mins** **25 mins** **40 mins**

The SiO_2 interface layer: UV Annealing



As deposited **15 mins** **25 mins** **40 mins**

…….can the interfacial oxide be reduced ?

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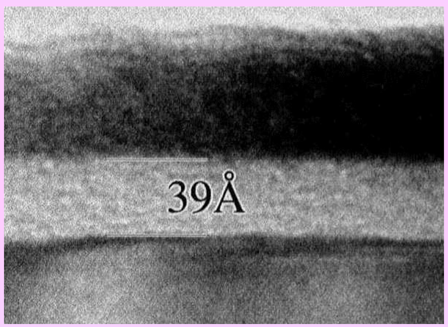
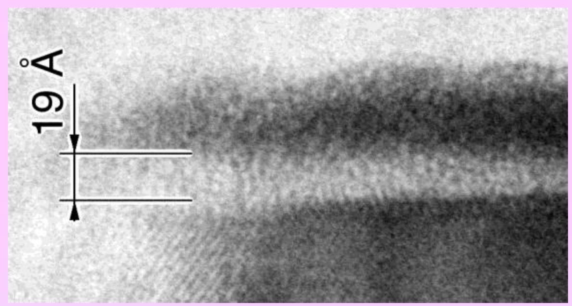
Suppression of interface oxide by Pre-deposition UV-anneal in N_2O

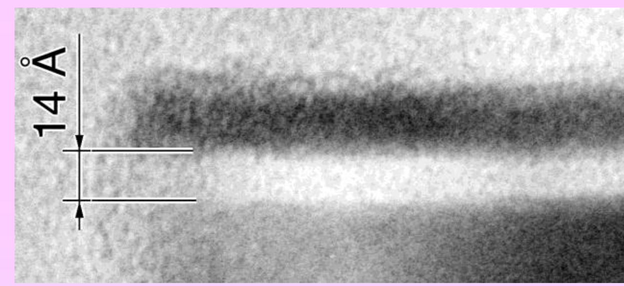
0 minutes



10 minutes

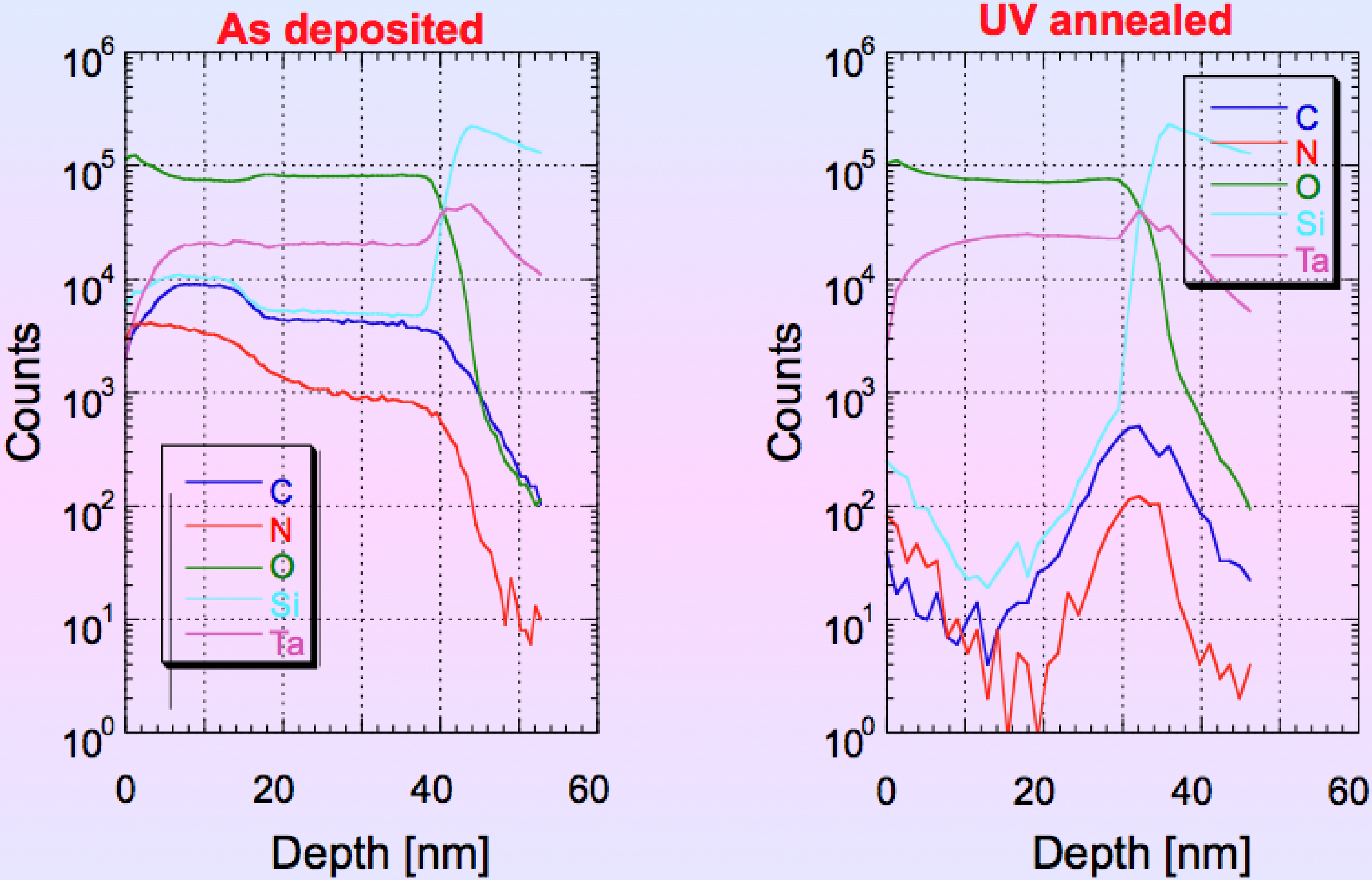


20 minutes



- Demonstrated previously, BUT typically T > 800^{o}C
- Pre photo-CVD at 350^{o}C

SIMS of photo-CVD Ta_2O_5 films



- **Reduction of C, N and Si after UV anneal**
  - No pile-up at Si - Ta_2O_5 interface or in bulk Si

Comparison of leakage current densities in Ta_2O_5 films obtained by different methods

	CVD[1]		Plasma - CVD[2]		Photo - CVD (our work)[3]	
	as-deposited	**annealing**	as-deposited	**annealing**	as-deposited	**annealing**
Leakage current density at 1 MV/cm (A/cm^2)	10^{-3}	**10^{-8}**	10^{-3}	**10^{-6}**	**2.19×10^{-5}**	**1.5×10^{-8}**
Deposited or annealed temp	350°C	**800°C**	500°C	**700°C**	350°C	**400°C**

Summary

- Snapshot overview of UV excimer lamp technology
- Example applications towards low temperature deposition of high quality electronic films demonstrated

  Rapid photo-oxidation

  Photo-deposition of dielectrics

  Metallization & nanocrystalline formation

  Surface modification & patterning

  NC-embedded matrices

- Applications in many other areas

  Surface modification, crystallisation

  Packaging

  Pollution control & Water treatment

  Curing of Paints, Varnishes, Coatings,

  Dry lithography, Printing

  Biological/Medical…..

Thank you for your attention !