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INTRODUCTORY OVERVIEW TO: DEPOSITION OF AMORPHOUS SILICON BY VERY-HIGH-FREQUENCY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION

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INTRODUCTORY OVERVIEW TO:

DEPOSITION OF AMORPHOUS SILICON BY VERY-HIGH-FREQUENCY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION

(ie a-Si:H by vhf PECVD)

Motivation: Increase rate of deposition of amorphous silicon whilst maintaining film quality - reduce cost of solar cells.

Structure:

INTRODUCTION

PLASMA PROPERTIES

PLASMA CHEMISTRY

POSSIBLE PLASMA DIAGNOSTICS

INTRODUCTION

AIM: Increase deposition rate R from industrial 0.3 nm/s to 2-3 nm/s without loss of film quality - by operating at 'optimum frequency' of the radio-frequency plasma. Currently, in industrial production, it takes about 1 minute to fabricate the p and n layers, but 30 minutes for the intrinsic amorphous silicon layer.

Industrial, Scientific and Medical (ISM) agreed frequency for high power sources is 13.56MHz. Almost all reported experiments work at this frequency.

a-Si:H better than crystalline silicon c-Si
c-Si is more efficient for solar cells, but is fabricated in a high temperature process.
Pay-back time for c-Si cell is 6.3 years
Pay-back time for a-Si:H cell is 2.2 years.
Also, a-Si:H can be deposited on any substrate, and on large surfaces.

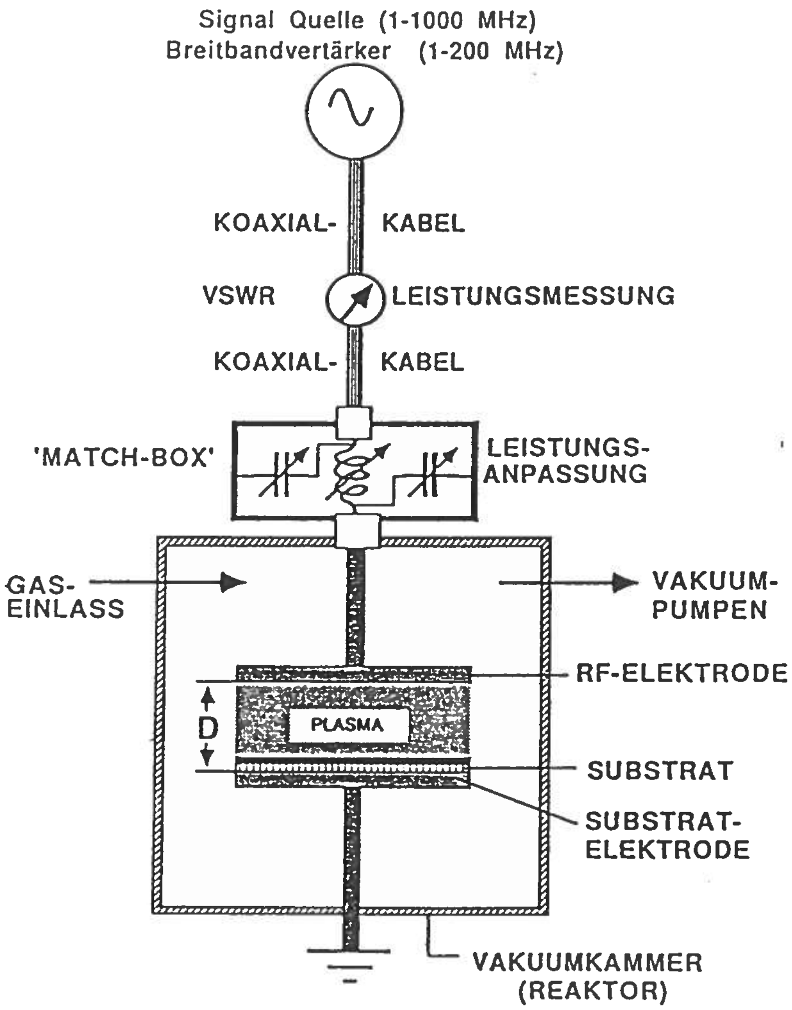
Plasma Enhanced Chemical Vapour Deposition (PECVD) better than Chemical Vapour Deposition (CVD)
PECVD is a low temperature process. High energy electrons and low energy molecules create exotic radicals at room temperature.

Much is not known:
Which radicals are important?
Neutrals or ions?
What plasma parameters should be optimised? - Physics.
What is a useful process monitor? - Industry.

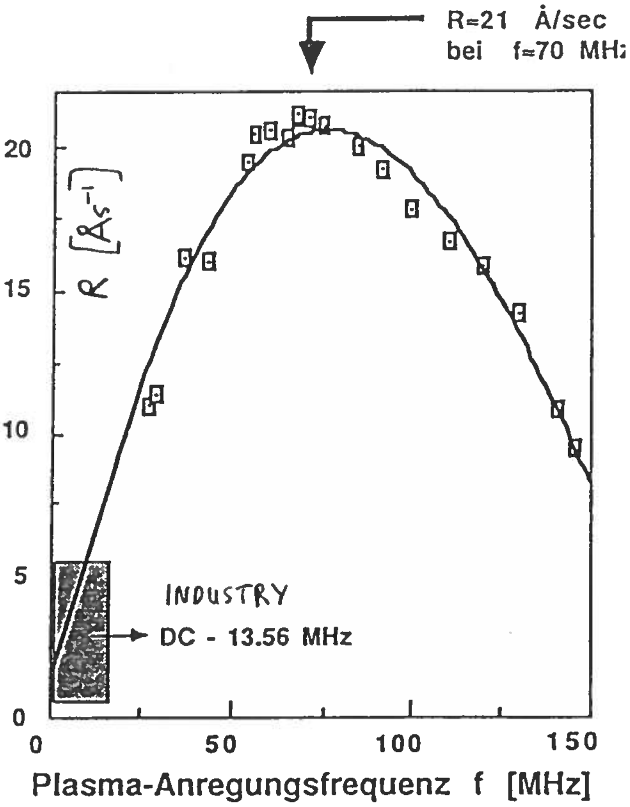
Figures on following page:

a) Schematic of the IMT Neuchâtel reactor. An rf source (<100W, 1 - 1000MHz) is applied via a matching circuit to two electrodes, producing a capacitative discharge. The source gas silane (SiH_4) is dissociated and ionised by electron impact in the plasma, and some of radicals drift toward the glass substrate which is placed on the grounded electrode, thus forming a deposit of amorphous silicon.
b) Deposition rate v frequency as measured at IMT Neuchâtel.

LABOR VHF-GD SYSTEM



ABSCHEIDUNGSRATE R(f)

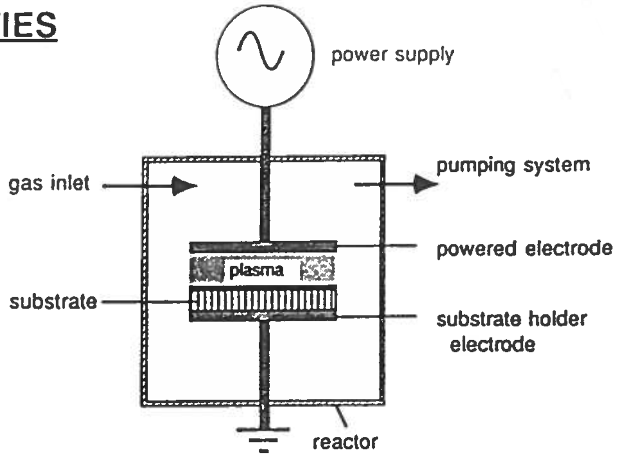


NB

No.		Perceived Risk	Perceived Benefit
1.	Solar Electric Power	12	56
2.	Jogging	14	65
3.	Sunbathing	20	49
4.	Cosmetics	20	49
5.	Roller Coasters	20	33
6.	Marijuana	21	53
7.	Surfing	21	41
8.	Fluorescent Lights	21	46
9.	Earth Orbit Satellite	22	54
10.	Recreational Boating	22	45
11.	Boxing	23	34
12.	Mushroom Hunting	23	32
13.	Hair Dyes	23	28
14.	Water Fluoridation	24	44
15.	Vaccinations	24	77
16.	Bicycles	24	68
17.	Space Exploration	25	51
18.	Downhill Skiing	26	57
19.	Home Appliances	26	72
20.	Swimming Pools	26	57
21.	Non-nuclear Electric Power	26	75
22.	Skyscrapers	26	39
23.	Scuba Diving	26	41
24.	Skateboards	27	37
25.	Christmas Tree Lights	27	44
26.	Bridges	27	69
27.	Mountain Climbing	28	47
28.	Tractors	29	61
29.	Food Coloring	29	19
30.	Railroads	29	48
31.	Home Gas Furnaces	29	49
32.	Anesthetics	29	55
33.	Pregnancy, Childbirth	30	60
34.	Antibiotics	30	68
35.	Football	30	54
36.	Hydroelectric Power	30	66
37.	Caffeine	30	42
38.	General Aviation	30	39
39.	Fireworks	31	42
40.	Commercial Aviation	31	54
41.	Aspirin	31	63
42.	Dams	31	64
43.	Jumbo Jets	32	48
44.	SST	33	30
45.	Hunting	33	47
46.	Home Power Tools	33	52
47.	Saccharin	35	25
48.	Laetrile	35	30
49.	Power Lawn Mowers	35	39
50.	Microwave Ovens	36	34
51.	Sodium Nitrite	38	31
52.	Food Irradiation	39	42
53.	Fossil Electric Power	40	65
54.	Prescription Drugs	41	73
55.	DNA Research	41	41
56.	Food Preservatives	42	36
57.	Lasers	42	34
58.	Police Work	43	75
59.	Motorcycles	43	43
60.	Fire Fighting	44	83
61.	Diagnostic X Rays	44	54
62.	Dynamite	47	30
63.	Surgery	48	64
64.	Valium	48	37
65.	Chemical Disinfectants	49	47
66.	Liquid Natural Gas	50	56
67.	Asbestos	51	51
68.	Oral Contraceptives	51	67
69.	Darvon	52	38
70.	Radiation Therapy	53	36
71.	Morphine	53	31
72.	Open-Heart Surgery	53	50
73.	Amphetamines	55	27
74.	Motor Vehicles	55	76
75.	Chemical Fertilizers	55	48
76.	Alcoholic Beverages	57	49
77.	Barbiturates	57	27
78.	Nerve Gas	60	7
79.	National Defense	61	58
80.	Heroin	63	17
81.	Terrorism	66	6
82.	Smoking	68	24
83.	Herbicides	69	33
84.	Pesticides	71	38
85.	Nuclear Power	72	36
86.	Crime	73	9
87.	Handguns	76	27
88.	DDT	76	26
89.	Warfare	78	31
90.	Nuclear Weapons	78	27

RISK & BENEFIT JUDGEMENT OF PUBLIC (NB American)

PLASMA PROPERTIES



Silane SiH_4 => Plasma Chemistry => Exhaust

Electrode diameter 135mm
Separation 10-50mm

Pure Silane used (no gas mixtures)
Continuous flow 20 sccm = 0,333 mbar.l/s (feedback controlled)
Pressure 0,2 mbar (feedback controlled)
Molecule residence time 1s approx.
Total Power 10W approx.

Above values are control parameters in the Institut de Microtechnique (IMT) Neuchâtel experiment.

Values below are typical measurements on 13.56 MHz reactors reported in the literature. Plasma parameters are not known for the vhf domain in the IMT reactor - this is the task of CRPP, EPFL. Figures may therefore *not* be representative of the IMT plasma

* SiH_4 density $n_g = 2.\ 10^{21}\ m^{-3}$ (mfp about 0.5mm)

* Weakly ionised $\alpha = n_e / n_g = 10^{-4}$ therefore *electron-neutral collisions dominate transport and radical production.* Debye length about 0,06mm.

* Neutral dissociation products about 1% of silane parent molecule density, ie:

(SiH_4) :	$(\Sigma\ Si_nH_m, H, H_2)$:	$(\Sigma$ ions$)$ = $1 : 10^{-2} : 10^{-4}$
source gas	neutral products	ionised products

* Plasma frequencies $f_{pi} = 7$ MHz $< f_{rf} = 70$ MHz $< f_{pe} = 1.55$ GHz

ie ions frozen and electrons mobile during an rf period.

* Electron-neutral momentum exchange frequency about 50 MHz.

* Primary reaction $e + SiH_4$ => products
* Secondary reactions products + SiH_4 => products'

(NB product + product' reactions are rare because SiH_4 dominates - almost all reactions occur with SiH_4)

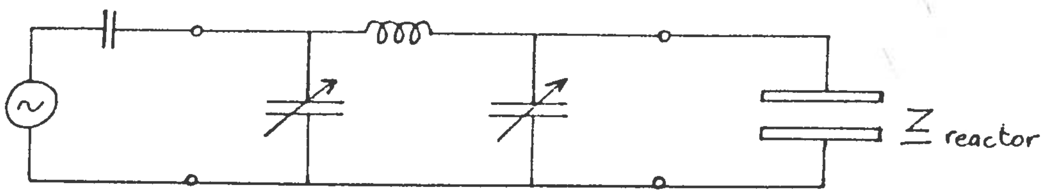
* NOT in Local Thermodynamic Equilibrium:
T_{gas} = 300K, T_e = 2eV = 20'000K, tail at 50eV

* Rf discharge more efficient at coupling energy to gas than dc discharge, eg for same apparatus:
dc 900V gave 0.02 Wcm^{-2} whereas
rf 200Vpp gave 0.05 Wcm^{-2}.

* There are 3 proposed mechanisms for energy transfer to electrons in the plasma:
i) Elastic collisions perturb the in-phase oscillations in the electric field allowing the electron to gain energy until an inelastic collision occurs.
ii) Secondary electrons from the film surface are accelerated through the sheath potential into the plasma (beam electrons)
iii) Electrons are reflected from the oscillating sheath boundary and can gain energy (wave-riding electrons).
Changing the rf frequency may well change the relative contibution and hence the discharge physics.

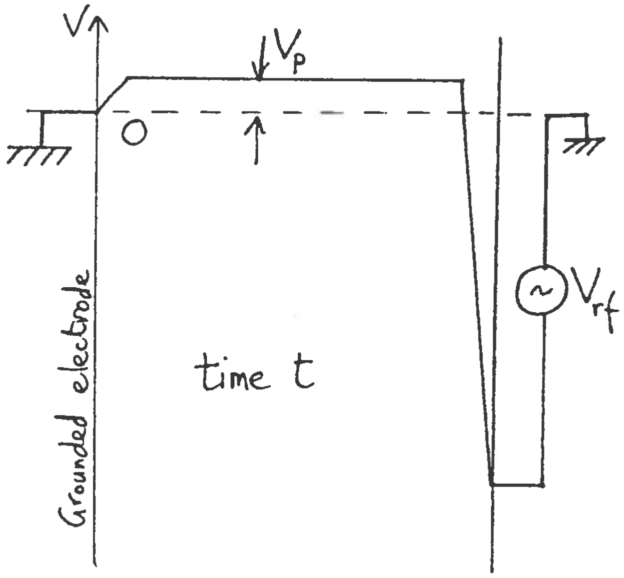
* A practical inconvenience of high frequency for large surface machines is that the free space wavelength approaches the machine dimensions, with attendant phasing problems.

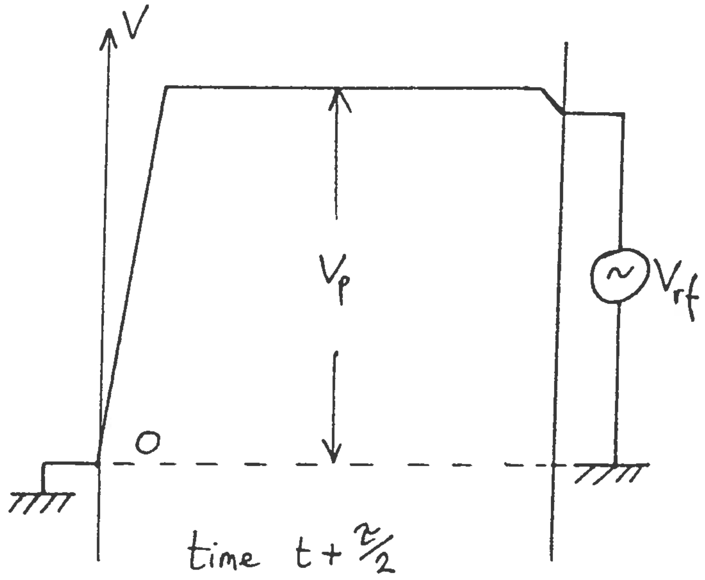
* SHEATH POTENTIALS
- determine ion energy impact damage/sputtering on the film
- beneficial for dehydrogenisation?



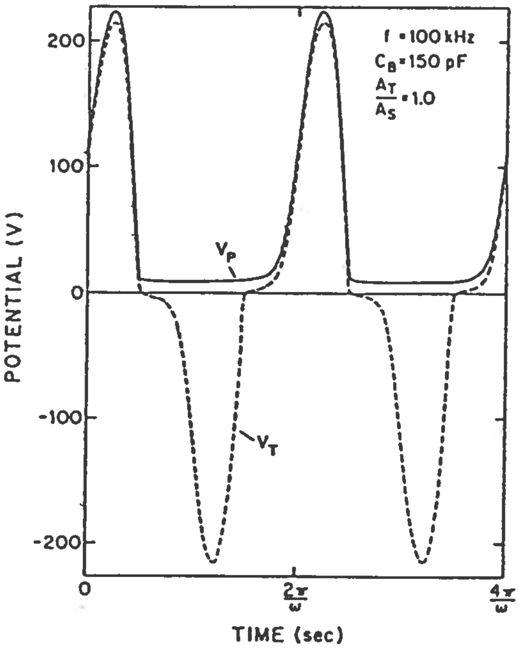
Π matching circuit

* For symmetric electrodes, the plasma/electrode potential must be the same for each electrode. Because one electrode is earthed, V_p varies by V_{rf} approx. (Rf potentials 200V pp >> plasma potentials V_p about 30V):



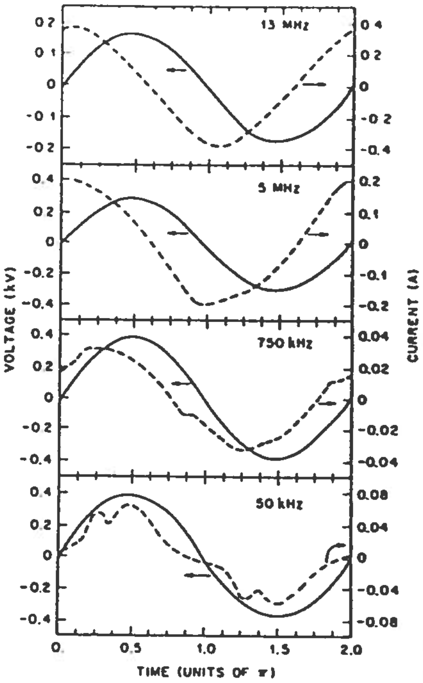


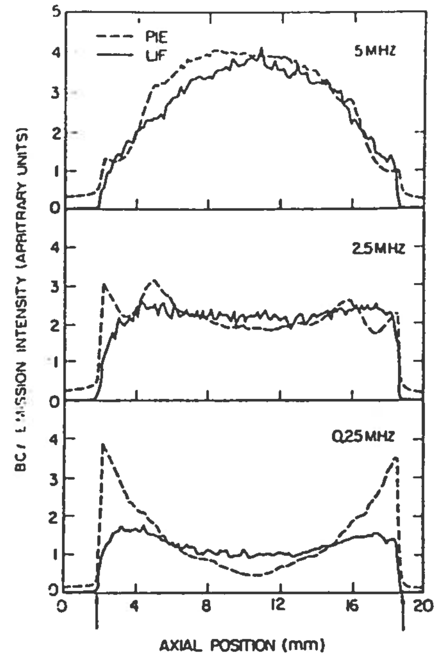
* No electrical difference between electrodes, but normally the substrate is on the grounded electrode:



Calculated waveforms of the voltage V_T across the plasma reactor and the plasma potential V_p for equal areas of the target and substrate electrodes.

* As frequency increases, reactor impedance becomes more capacitative (ions stationary at vhf, so no conduction current), therefore less power lost in the sheaths - implies better coupling of power to the bulk plasma.





Visible Emission Profiles

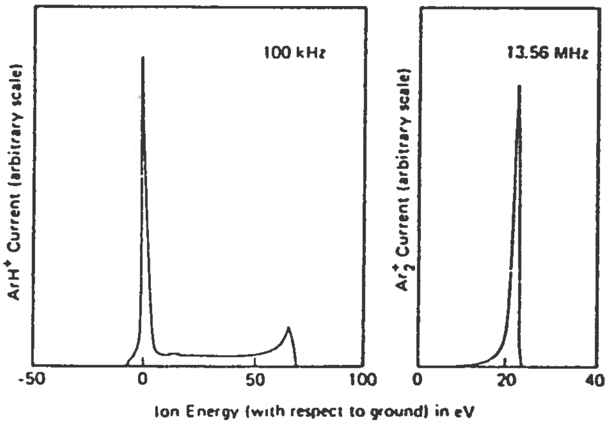
* Direct proof for efficiency of coupling at vhf from visible emission profiles: plasma emission increases in centre of discharge for higher frequency - power into gas, not into sheaths.

* Also, since sheath potentials α 1/ωC, sheath potentials fall as frequency increases.

* ION ENERGY DISTRIBUTION

At low frequency, ion energy varies between 0 and V_{rf} (depending on phase of field on entry of ion to sheath).

At high frequency, ions see only the average sheath potential = $V_{rf}/2$, and since $V_{rf} >> eT_i$, there is a monochromatic ion energy distribution arriving at the film surface.

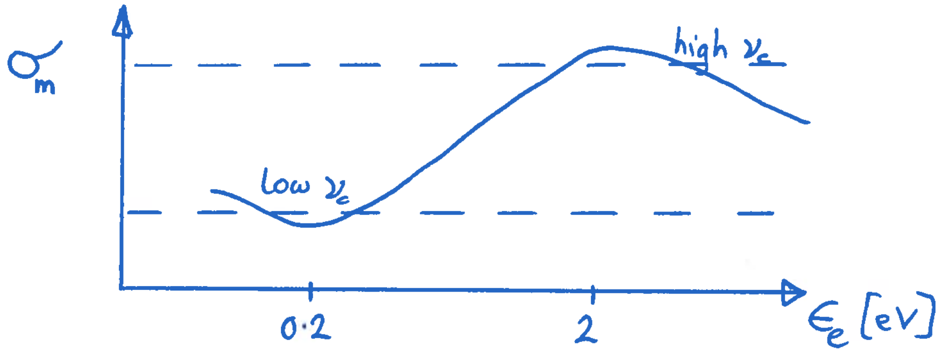


. Energy distributions of ions extracted through the ground plane of a planar diode rf glow discharge system with 100-kHz and 13.56-MHz excitation frequencies. Argon pressure = 50 mTorr.

*ELECTRON ENERGY DISTRIBUTION

For low ionisation $\alpha = 10^{-4}$, strong deviations from Maxwell distribution due to dissociation, excitation and ionisation. Electron-neutral collisions dominate, electron-electron thermalisation absent. Silane dissociation 2-7 eV, dissociative ionisation > 11eV.

Trend of silane cross-section for momentum transfer, σ_m, v. frequency:



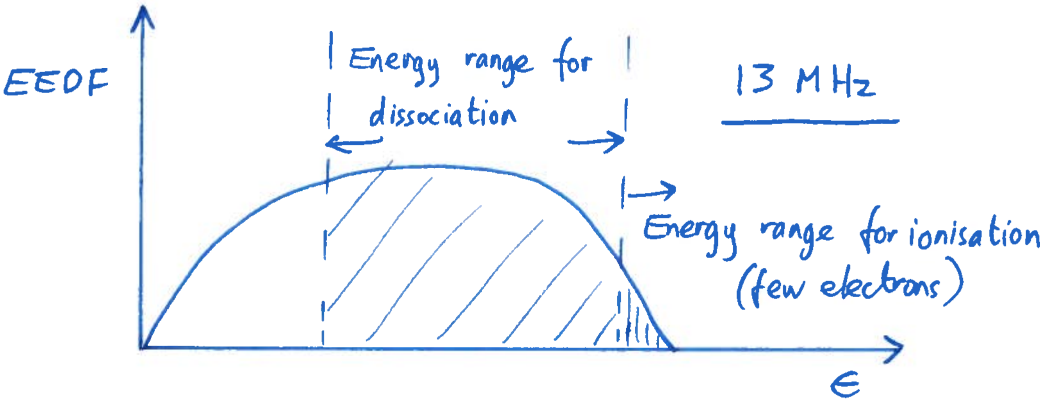
Note that momentum transfer collision frequency $\nu_c \alpha \sigma_m . T_e^{.5}$

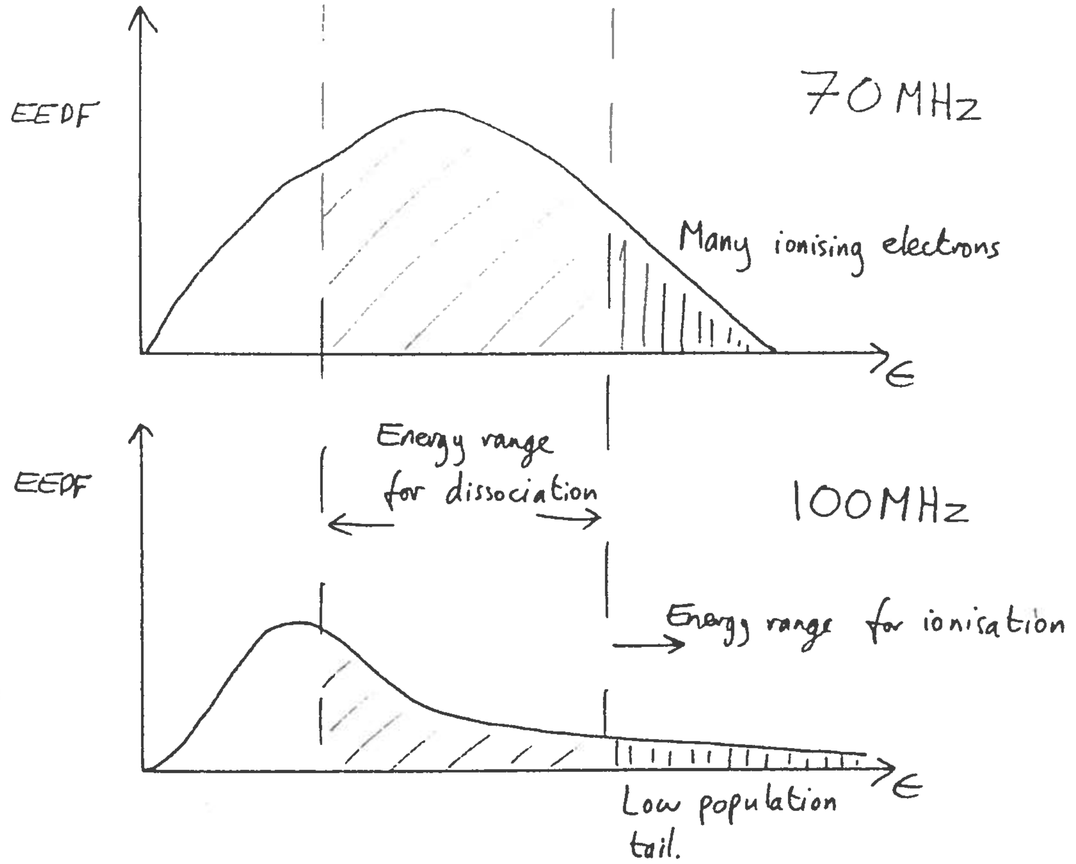
Energy transfer term in Boltzmann equation goes as $\nu_c E_{rf}^2 / (\nu_c^2 + \omega_{rf}^2)$, therefore maximum electron-silane energy transfer efficiency occurs when $\omega_{rf} = \nu_c$, ie strongest transfer to silane from electrons whose energy corresponds to a collision frequency equal to the rf driving frequency.

At low rf frequency: low ν_c corresponds to low-energy electrons, ie low ω_{rf} couples to electrons with energy below ionisation threshold ie low ionisation efficiency at low ω_{rf}.

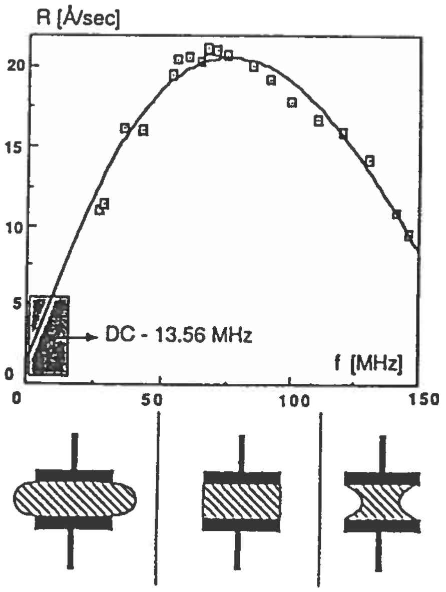
At high rf frequency: high ν_c corresponds to high-energy electrons, ie high ω_{rf} couples to electrons with energy above ionisation threshold. But their population is low at high energy ie *low* ionisation efficiency at high ω_{rf}.

* Imagined electron energy distribution functions for 'low', 'medium, and 'high' frequency rf supply:





- There is an optimum frequency for high ionisation (and, consequently, high electron density leading to a high radical production); this may be an explanation for the Neuchâtel observation of a maximum in the deposition rate v. frequency curve at constant rf power:



Note that the plasma at 80MHz was the easiest to start, required the least power to maintain, and had the most uniform confinement between the electrodes.

SUMMARY - FREQUENCY VARIATION

Low f (100kHz) < f_{pi} (7MHz) < High f (70MHz) << f_{pe}

Resistive sheaths	Capacitative sheaths
High sheath voltages - Inefficient power transfer	Low sheath voltages - Efficient power transfer
Good for etching	Low surface damage
A range of ion energies	Monochromatic ion energy
Low electron density	High electron density, high radical density
	Modification of distribution of energy to bulk, beam, and wave-riding electrons

Frequency increase beneficial (70 MHz optimum?)
- unexplored domain, lots of scope.

PLASMA CHEMISTRY

Which species deposit the silicon? Ionic? Neutral radicals (Si, SiH, SiH_2, SiH_3,... Si_2H_6,.....Si_3H_8.....)?

Which conditions for good film quality (eg substrate temperature)?

How to increase deposition rate?

PROCESS OF ELIMINATION

* Neutral flux = 1'000 X positive ion flux, so neutrals dominate deposition. NB although neutrals are responsible for Si transport to the film, ions, by virtue of their high sputtering yield, may yet be the rate-limiting factor for the deposition rate.

* Negative ions are trapped between the sheath potential barriers and don't reach the film surface. However, they might accumulate and affect bulk plasma chemistry - micowave measurements of free electron density would also be underestimates of the total ion density.

* Silane itself does not react with a surface for $T_{substrate} < 350^oC$ (usually around 280^oC).

* Therefore neutral dissociation products of e + SiH_4 are responsible for silicon transport to the growing film. The relative importance of the different dissociation branches remains unknown, but since the production of free silicon and SiH is so small, the main contenders are SiH_2 and SiH_3.

THE ARGUMENT FOR SiH_3 AS THE DOMINANT RADICAL.

eg Gallagher A. J Appl Phys 43 544 (1983)
J Appl Phys 63 2406 (1988)
Solar Cells 21 147 (1987)

Possible Primary reactions are:				Comment according to 'SiH$_3$' group:
e + SiH_4	=>	$SiH_2 + H_2 + e$	(2.6eV)	x H_2 unlikely to form*
		$SiH_3 + H + e$	(4.3eV)	25% branching ratio

$Si + 2H_2 + e$	(4.7eV)	x H_2 unlikely to form*
$SiH + H + H_2 + e$	(6.2eV)	4% branching ratio
$SiH_2 + 2H + e$	(7.2eV)	71% branching ratio
$SiH + 3H + e$	(10.7eV)	x energy too high
$Si + 4H + e$	(11.7eV)	x energy too high

*Some authors favour the first reaction yielding SiH_2. However this thermodynamic reasoning does not really apply to the dissociation of a molecule raised to a repulsive state by electron impact. In the explosive expansion of the silane molecule, the reforming of an H-H bond is unlikely (the H atoms are already initially at a distance larger than the H-H equilibrium bond length).

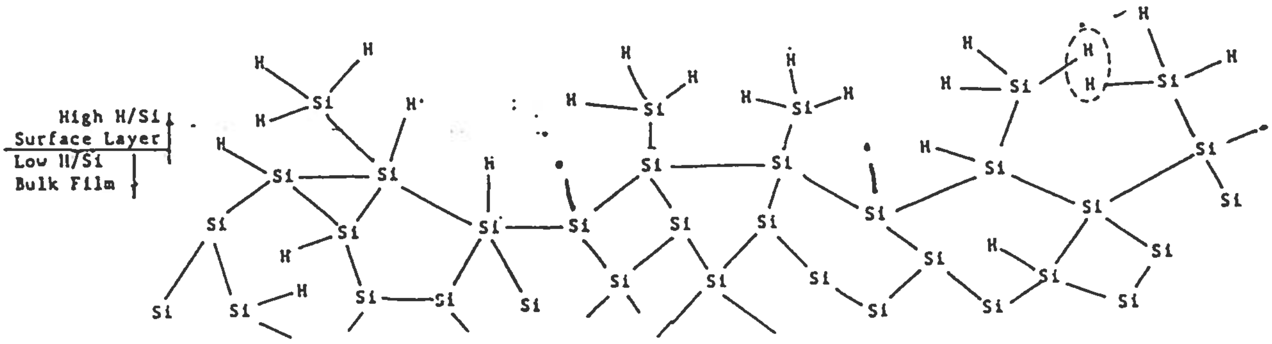
Then we need only consider <u>secondary reactions</u> with silane (see previous section):

$H + SiH_4 \Rightarrow H_2 + SiH_3$	FAST, SiH_3 produced
$SiH_2 + SiH_4 \Rightarrow Si_2H_6$	FAST, *SiH_2 lost* (mfp 3mm)
$SiH + SiH_4 \Rightarrow SiH_2 + SiH_3$	(in unimportant quantity)
$SiH_3 + SiH_4$	NO EXOTHERMIC REACTION, *SiH_3 not lost.*

These secondary reactions alter the branching ratio. It is claimed that: <u>98% of radicals reaching the film surface are SiH_3</u>.

<u>SURFACE CHEMISTRY</u>

The surface of the growing film will be hydrogen-covered:



- SiH_3 cannot, energetically, break a Si-H surface bond and insert itself.
- SiH_3 needs a 'free ' or 'dangling' silicon bond to attach to - denoted by =Si-·.
- Deposition rate, in this model, is then determined by the rate of 'dehydrogenisation'.

Dangling bond creation:

$$(\mathrm{SiH_3})_{gas} + (\mathrm{Si\text{-}H})_{surface} \Rightarrow (\mathrm{SiH_4})_{gas} + (\mathrm{{=}Si\text{-}{\cdot}{\cdot}})$$

and $$\mathrm{H} + (\mathrm{{=}Si\text{-}H}) \Rightarrow \mathrm{H_2} + (\mathrm{{=}Si\text{-}{\cdot}{\cdot}}),$$

ie reactions using SiH_3 and free H atoms produced from primary and secondary reactions can produce dangling bonds ready for SiH_3 insertion.

SiH_3 surface reactions:

SiH_3 is weakly physisorbed as $SiHSiH_3$ complex and migrates across the surface until it is either lost:

$$(\mathrm{SiH_3})_{adsorbed} + (\mathrm{SiH_3})_{adsorbed} \Rightarrow (\mathrm{Si_2H_6})_{gas}$$

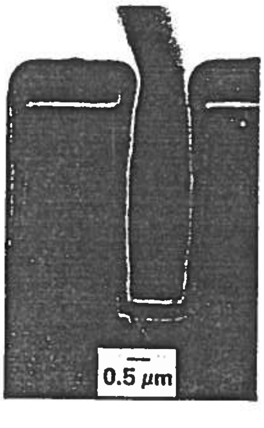
or incorporated: $(\mathrm{SiH_3})_{adsorbed} + (\mathrm{{=}Si\text{-}{\cdot}{\cdot}}) \Rightarrow (\mathrm{{=}SiH_3})_{film}$ *film growth.*

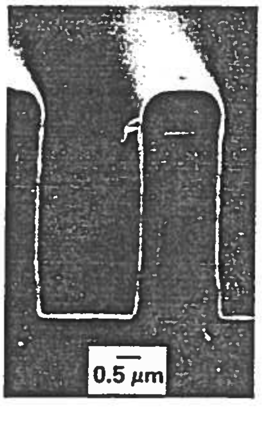
Surface Morphology Studies:

Note that SiH_3 incorporates into the film only where free bonds exist whereas Si, SiH, SiH_2 can exothermically stick on any surface location by insertion into a Si-H bond. The former is reminiscent of Chemical Vapour Deposition (CVD) (characterised by migration), the latter resembles Physical Vapour Deposition (PVD) (characterised by line-of-sight deposition).

See Tsai J Appl Phys 59 2998 (1986) and 64 699 (1988), study of a-Si:H deposition onto a patterned substrate:

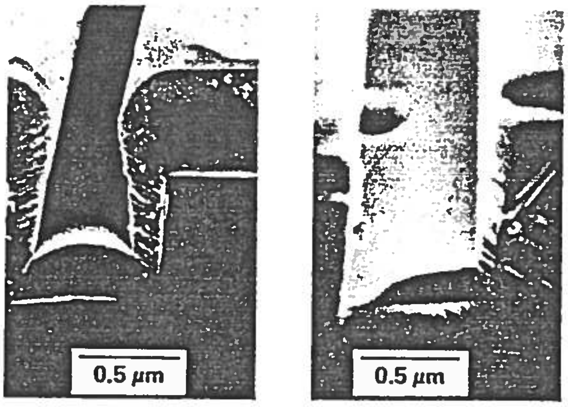
For conditions favourable to SiH_3 production (see later):
- Deposition similar to CVD
- Uniform, homogeneous surface coverage
- Low sticking-coefficient radical deposition
- Low power, pure silane discharge
- Substrate temperature around 230°C
- Produces device quality amorphous silicon.



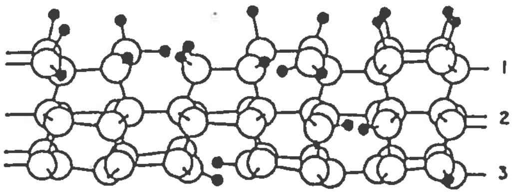


For conditions favourable to SiH_2 production:

- -Deposition similar to PVD
- -Sticking-coefficient =1
- -Shadow, non-uniform coverage
- -Columnar structure; rough, porous surface with voids in the film
- -High defect density
- -Produces poor quality films

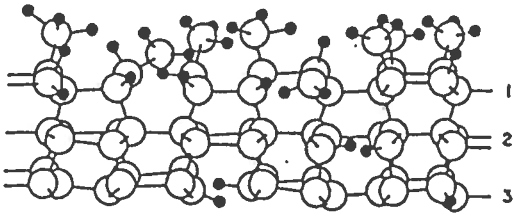


Also, argon sputtering followed by mass spectrometry (Lin, J Appl Phys <u>64</u> 188 (1988)) shows that SiH_3 groups are attached to the surface for plasma conditions giving optimal a-Si:H quality:



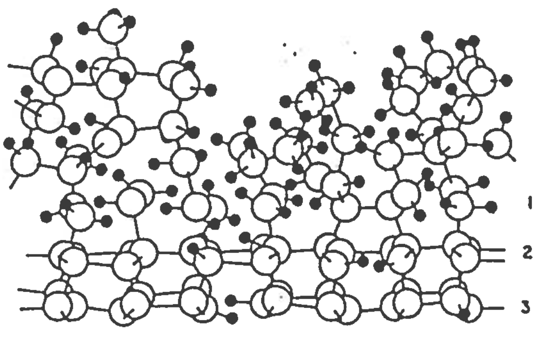
(a)

1·5 H per Si
Not found experimentally
for good films.



(b)

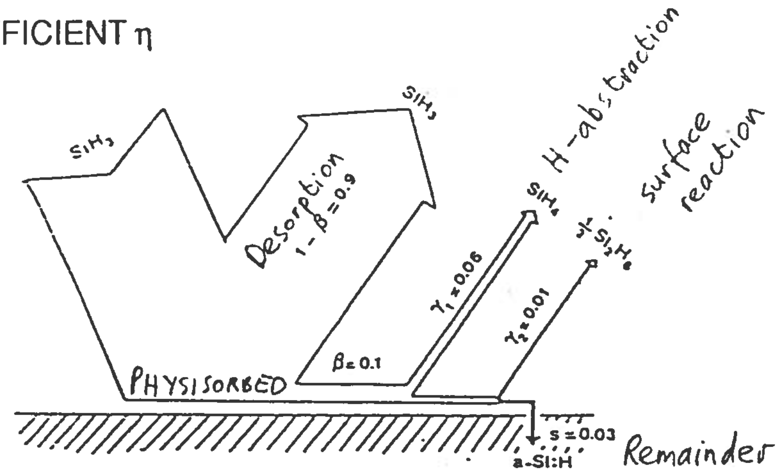
SiH_3 groups attached (?)
2H per Si (top monolayer)
$T_{substrate} = 240\,°C$
As measured for good films.



(c)

5 monolayers of H-rich a-Si:H.
Long attached chains of SiH_3 / SiH_2 (?)
Poor film quality
$T_{substrate} = \underline{25°C}$.

SiH_3 STICKING COEFFICIENT η



Remainder incorporated into film.

Some groups claim that eg SiH_2, SiH can become important for film growth because:

$\eta(SiH_2, SiH) = 1, >> \eta(SiH_3)$, whose value is uncertain.

In the literature, the range $0,01 < \eta(SiH_3) < 0.7$ can be found. Alan Gallagher claims $\eta(SiH_3) = 0.3$.

FILM STOCHIOMETRY

The top few monolayers have $(H)/(Si) = 3$ approx. as explained above.
The bulk material, however, has a much higher concentration of silicon, $(H)/(Si) = 0.2$ approx.
The loss of hydrogen is proposed to occur via cross-bonding:

$$(\equiv Si\text{-}H)_{film} + (\equiv Si\text{-}\cdot)_{film} \Rightarrow (Si\text{-}Si)_{film} + H_{gas}$$

and

$$(\equiv Si\text{-}H)_{film} + (\equiv Si\text{-}H)_{film} \Rightarrow (Si\text{-}Si) + (H_2)_{gas}$$

(The second reaction can only occur below the surface: H_2 diffuses out)

PROCESS OPTIMISATION STUDIES

* <u>Effect of dilution of SiH_4 with other gases, and rf power dependance.</u>

Motivation: i) to economise on SiH_4, ii) to attempt to reduce dust (macromolecules) originally thought to be caused by too many secondary reactions with SiH_4. Dust causes a puncture in a film leading to poor electrical properties and is a major obstacle in industrial production of device quality amorphous silicon.

Results of empirical work (eg Knights, Appl Phys Lett 38 331 (1981)):
"Best quality film with low rf power and pure silane"

Explanation on current understanding: Dilution with other gases (except possibly hydrogen, Vanier, J Appl Phys 56 1812 (1984)) reduces the probabilty of scavenging of SiH and SiH_2 by SiH_4, thereby allowing these high-sticking-coefficient species to reach the surface. High rf power has the same effect by depleting the source gas silane. Therefore we have the dilemma:

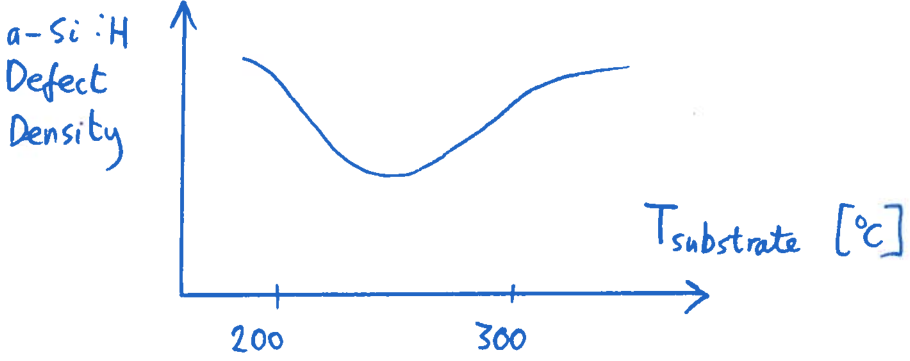
Pure silane, low Prf = good film, low powder, but low deposition rate.
Pure silane, high Prf = bad film, high powder, high deposition rate.
Diluted silane = bad film, high powder, low deposition rate.

Empirically (Curtins et al, Pl Chem & Pl Proc 7 267 (1987)), frequencies higher than 13.56MHz (used in the above experiments) permit high deposition rates whilst maintaining good film quality. However, an understanding is lacking and a plasma diagnostic programme (CRPP, EPFL) is necessary to help resolve the problem.

* Substrate Temperature

An elevated substrate temperature is necessary for radical surface mobility (migration of attached SiH_3 complexes), bond manoeuvrability and H, H_2 diffusion from the surface and the bulk material. Attention must also be paid to the problem of film/substrate adhesion (surface stresses, different thermal expansion coefficients).

For $T_{sub} < 200^oC$, bond cross-linking is inhibited (insufficient mobility)
For $T_{sub} > 300^oC$, H diffuses out of a-Si:H leaving internal defects.
T_{sub} around 240°C seems to be optimum.



SUMMARY OF SiH_3 GROUPS

Trend of: Increasing rf power
Dilution of silane
Lower flow rate
Lower pressure
Higher deposition rate (13.56MHz)
(all causing higher silane depletion)
leads from:

SiH_3 dominated mass transport	to	SiH_2 dominated mass transport
High quality a-Si:H	to	Low quality film (μc-Si:H)
CVD-like deposition	to	PVD-like deposition
(low sticking-coefft. radicals)	to	(high sticking-coefft. radicals)
Uniform coverage	to	Shadow deposition
Smooth surface	to	Rough, columnar surface with voids

THE ARGUMENT FOR SiH_2 AS THE DOMINANT RADICAL

It is claimed that $SiH_4 + e \Rightarrow SiH_2 + H_2 + e$

is the dominant reaction (eg Veprek, Pl Chem & Pl Proc 9 29S (1989) and Ensslen and Veprek, Pl Chem & Pl Proc 7 139 (1987)). However, in a compendium of over 40 silane dissociation channels, Kushner (J Appl Phys 63 2532 (1988)) excludes this reaction, presumably for the reasons given in the SiH_3 section above, reserving this reaction channel for 'homogeneous pyrolysis' which is 'negligible for substrate temperatures used in PECVD'.

Since $SiH_2 + SiH_4 \Rightarrow Si_2H_6$
is rapid, advocates of the above reaction are obliged to claim that Si_2H_6 is the depositing radical, whereas the rival group state that Si_2H_6 is a saturated molecule having no reaction with the a-Si:H surface. The SiH_2 group, on the other hand, points out that the low density and low sticking-coefficient of SiH_3 eliminate it as a candidate for the observed rate of growth. For the present, the growth mechanism remains controversial.

POSSIBLE PLASMA DIAGNOSTICS

The diagnostics in the following list will be considered in turn. The diagnostics underlined are possible candidates for an experiment at CRPP, EPFL.

1 Optical Emission Spectroscopy
2 Reflectometry
3 Laser-induced fluorescence
4 Mie scattering
5 Microwave interferometry
6 Infrared thermometry
7 Electrical measurements
8 Langmuir, plasma potential probes
9 Quadrupole mass spectrometry
10 Electrostatic grid energy analysers
11 Infrared laser diode absorption spectroscopy
12 Ellipsometry
13 Laser diffraction of layers on fibres

* * * * * *

1 OPTICAL EMISSION SPECTROSCOPY

Only Si, Si^+, SiH, SiH^+, H and H_2 emit - unfortunately these are minority species. SiH_2 and SiH_3 have no known emission spectra. See table at end of report for main lines. Lines most often used in the literature are:

Atomic Si 288, 391nm
SiH blue, complicated vibrational bands 413 - 428nm
H, H_2 - useful for process monitoring?
Continuum H_2 - evidence for EEDF tail.
Impurity lines - monitoring of leaks, poor wall/substrate conditioning etc. Impurities have been shown to worsen the solar cell aging sensitivity (Staebler-Wronski effect).

At CRPP, at least measure SiH^* distribution in space and time. Versatility will be greatly enhanced with an Optical Multichannel Analyser (OMA).

2 REFLECTOMETRY with a He-Ne Laser
Gives in-process deposition rate, very useful for parameter scan programmes, but needs vertical access through electrodes.

3 LASER-INDUCED FLUORESCENCE
In the literature, and at CRPP, can measure neutral Si and SiH distributions. More exotic experiments include Coherent Anti-Stokes Raman Spectroscopy (CARS) and frequency-modulated absorption spectroscopy for SiH_2, as well as Laser Opto-Galvanic Spectroscopy - to be evaluated later.

4 MIE SCATTERING of He-Ne laser
- is the scattering of light by particles much larger than a wavelength. Very useful monitor of dust production, crucial for industrial-quality applications. Relatively easy to install at CRPP.

5 MICROWAVE INTERFEROMETRY
-for free-electron density, using eg double-pass interferometer. Expertise and hardware exists at CRPP.

6 INFRARED THERMOMETRY
Non-contact thermometry of substrate surface would eliminate errors in the measurement of T_{sub} due to thermal gradients in the reactor. Needs vertical viewing. In practice, complicated by uncertainty in emissivity.

7 ELECTRICAL MEASUREMENTS
-for electrode rf potential, current and power. Very important, but difficult at variable high frequency (10-100MHz). Will purchase commercial probes for CRPP. Methods exist in the literature for bridges to measure plasma impedance.

8 LANGMUIR & PLASMA POTENTIAL PROBES
Simple to implement, but extremely difficult to interpret, especially at vhf. Probes used in silane plasmas become coated with silicon rendering them useless. There are several tricks one can use, but probes will probably be used at most as a check on plasma condition reproducibilty for inert gases at CRPP.

9 QUADRUPOLE MASS SPECTROMETRY

A measure of the gas composition at the exhaust relative to that injected provides the silane depletion fraction, a fundamental parameter for comparison with different reactors.

10 ELECTROSTATIC GRID ENERGY ANALYSERS

An arrangement of grids built into an electrode would allow an estimation of ion energies reaching the substrate from the plasma thus giving information on sheath potentials.

11 INFRARED LASER DIODE ABSORPTION SPECTROSCOPY

Can be used for SiH_2 and SiH_3 densities, but would require local experts and specialised equipment; this may prove to be impractical at CRPP.

12 ELLIPSOMETRY

Measures film thickness and stochiometry. The diagnostic is very expensive, requires oblique-angled observation ports and experienced operators for data interpretation. Since thickness will in principle be measured by much simpler reflectometry, and stochiometric post-process measurements are the domain of IMT Neuchâtel, CRPP will most likely not use ellipsometry.

13 LASER DIFFRACTION OF LAYERS ON FIBRES

Gallagher described a method of estimating deposition profiles in the plasma volume by constructing a network of fibres between the plates, using laser diffraction to measure the growing layer thickness. This experiment is for studying fundamental deposition physics in the plasma and there is much we can do to study the undiagnosed IMT-type plasma before confronting the complexity of these more exotic techniques at CRPP.

THE MOST AMBITIOUS INITIAL PROGRAMME WOULD ATTEMPT TO MEASURE:

Distribution of excited atoms Si*, SiH*
Distribution of ground state densities of Si and SiH
Deposition rate
Dust production
Electron density
Substrate surface temperature

Rf waveforms

Silane depletion fraction

- as a function of frequency and film quality. The effect of rf power modulation, different gas mixtures etc could also be studied.

Once any trends dependent on frequency become apparent, additional diagnostics can be considered.

Species	*Emission wavelength* λ (nm)	*Transition*	*Energy of emitting state above ground state* (eV)
Si	198 - 199	UV7	6.3
Si	206	UV52	6.8
Si	212	UV48	6.6
Si	221 - 222	UV3	5.6
Si	229 - 230	UV46	6.2
Si	244	UV45	5.9
Si	251 - 253	UV1	4.9
Si	263	UV83	6.6
Si	288	UV43	5.1
Si	299	1	5.0
Si	391	3	5.1
SiH	386 - 388	$A^2\Delta - X^2\Pi$	3.0
SiH	394 - 396	$A^2\Delta - X^2\Pi$	3.0
SiH	413 - 428	$A^2\Delta - X^2\Pi$	3.0
SiH^+	399	$A^1\Pi - X^1\Sigma$	3.1
H	434	$H\gamma$	13.0
H	486	$H\beta$	12.7
H	656	$H\alpha$	12.0
H_2	Continuum 160 - 500	$2s^3\Sigma - 2p^3\Sigma$	11.9
H_2	Many lines 368 - 835	$3d^1\Sigma - 2p^1\Sigma$ $3d^1\Pi - 2p^1\Sigma$ $3p^3\Pi - 2s^3\Sigma$ etc.	4.0 4.0 4.0
N_2	316	Second positive system, $C^3\Pi_u - B^3\Pi_g$	11.1
N_2	337	Second positive system, $C^3\Pi_u - B^3\Pi_g$	11.1
N_2	358	Second positive system, $C^3\Pi_u - B^3\Pi_g$	11.1
SiCl	281 - 282	$B'^2\Delta - X^2\Pi$	4.4
SiO	224	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	230	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	234	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	237	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	239	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	241	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	249	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	259	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	267	$A^1\Pi - X^1\Sigma^+$	5.3
SiO	269	$A^1\Pi - X^1\Sigma^+$	5.3
OH	306.4	$A^2\Sigma^+ - X^2\Pi$	4.1

From Kampas FJ & Griffith RW, Solar Cells 2 385 (1980)