Toxicology and Safety

MBE maintenance: safety management

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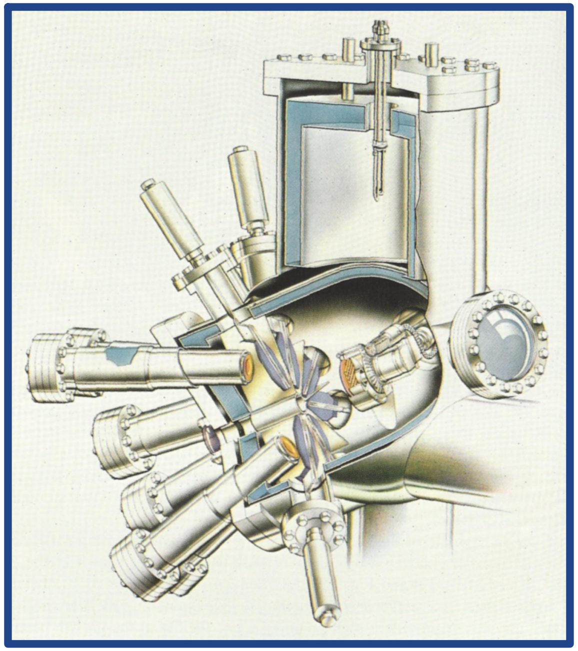


Outline

- III-V semiconductor materials
- Molecular beam epitaxy
- Hazardeous effects of P, As and their compounds
- Arsenide treatment during MBE maitenance
- Phosphorous handling and recovery for MBE systems
- Summary

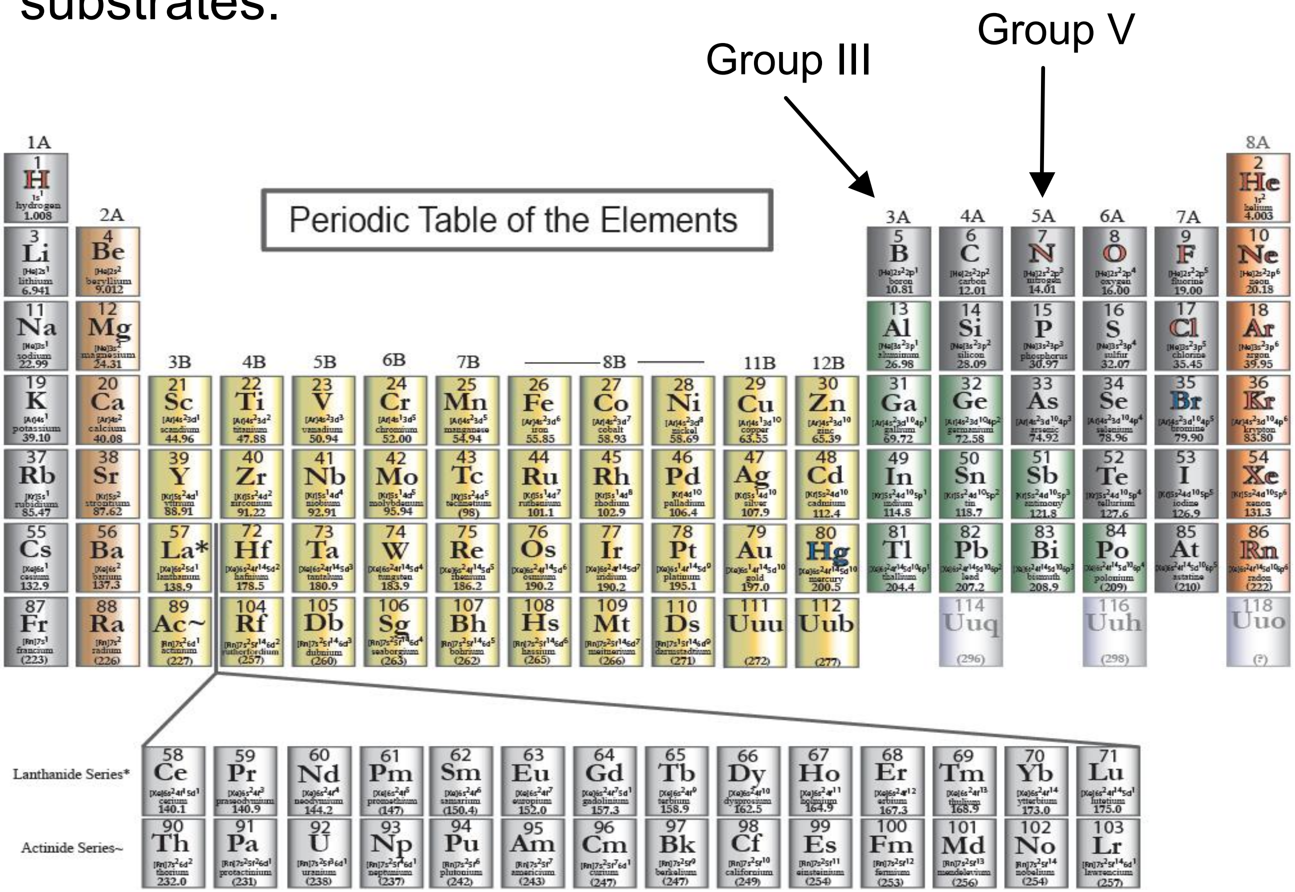
Semiconductor Materials used in MBEs: Overview

- **Group III and V** elements used for epitaxy on GaAs and InP substrates.

- **Major doping materials:** Be, C, Si

- **II-VI epitaxy** (Zn, Cd, Hg, S, Se, Te) on ZnSe

- **Group IV epitaxy** (Si, Ge)



Group III

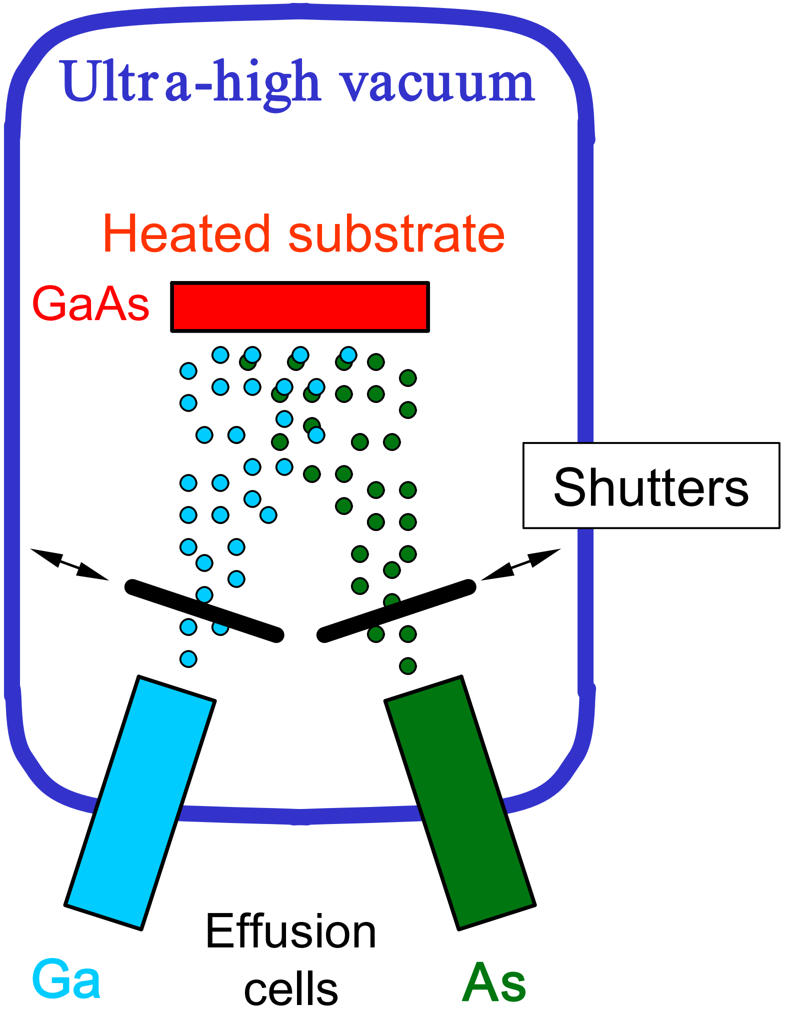
Group V

Periodic Table of the Elements

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	11B	12B	3A	4A	5A	6A	7A	8A
1 H hydrogen 1.008																	2 He helium 4.003
3 Li lithium 6.941	4 Be beryllium 9.012											5 B boron 10.81	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31											13 Al aluminum 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cl chlorine 35.45	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.88	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.39	31 Ga gallium 69.72	32 Ge germanium 72.58	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium (98)	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs cesium 132.9	56 Ba barium 137.3	57 La* lanthanum 138.9	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.9	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 190.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.5	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 208.9	84 Po polonium (209)	85 At astatine (210)	86 Rn radon (222)
87 Fr francium (223)	88 Ra radium (226)	89 Ac~ actinium (227)	104 Rf rutherfordium (257)	105 Db dubnium (260)	106 Sg seaborgium (263)	107 Bh bohrium (262)	108 Hs hassium (265)	109 Mt meitnerium (266)	110 Ds darmstadtium (271)	111 Uuu (272)	112 Uub (277)		114 Uuq (296)		116 Uuh (298)		118 Uuo (?)

Lanthanide Series*	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium (147)	62 Sm samarium (150.4)	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0
Actinide Series~	90 Th thorium 232.0	91 Pa protactinium (231)	92 U uranium (238)	93 Np neptunium (237)	94 Pu plutonium (242)	95 Am americium (243)	96 Cm curium (247)	97 Bk berkelium (247)	98 Cf californium (249)	99 Es einsteinium (254)	100 Fm fermium (253)	101 Md mendelevium (256)	102 No nobelium (254)	103 Lr lawrencium (257)

Principle of III-V Molecular Beam Epitaxy



- Epitaxy on heated substrates
- Source materials evaporated in effusion cells:
  → elemental Ga, In, Al, P, As, Sb
- Process in ultra-high vacuum
- Flux control by mechanical shutters
- **Some advantages** in material handling in comparison to MOCVD
  → solid materials, less toxic
  → low material consumption
- **Disadvantage:** Refilling and periodic maintenance necessary.

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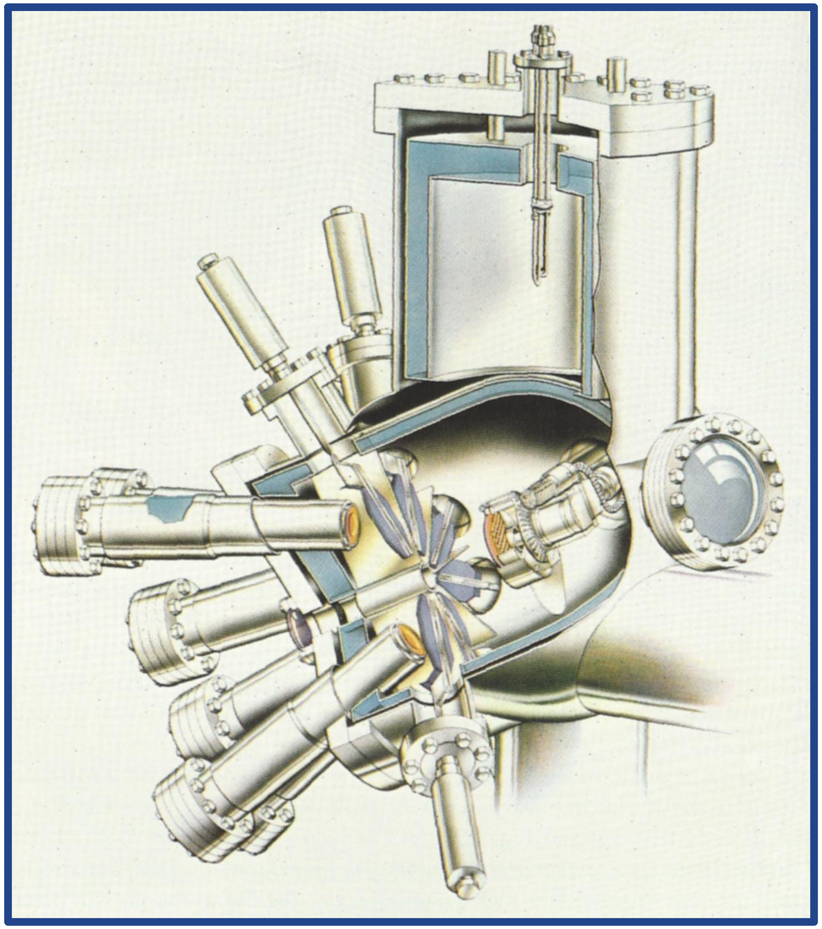
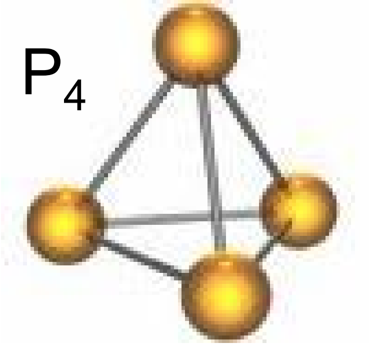
Molecular Beam Epitaxy: General Safety Concerns



- Usage of As and P
- White phosphorous – pyrophoric and toxic
- Possible oxidation – formation of toxic oxides
- Formation of hydrides (AsH_3 and PH_3) is also likely
- **No severe safety issue** during operation (some exception for P)
  → Phosphorous cold traps
- **Major safety concerns** during maintenance (system opening)
  → Personal protection
  → Air contamination control
  → Environment protection

Atomic and Molecular Phosphorous P, P_2, P_4



- red (amorphous) phosphorous is considered not to be toxic (formed by P_2, P). However, inhalation of dust may cause pneumonia.

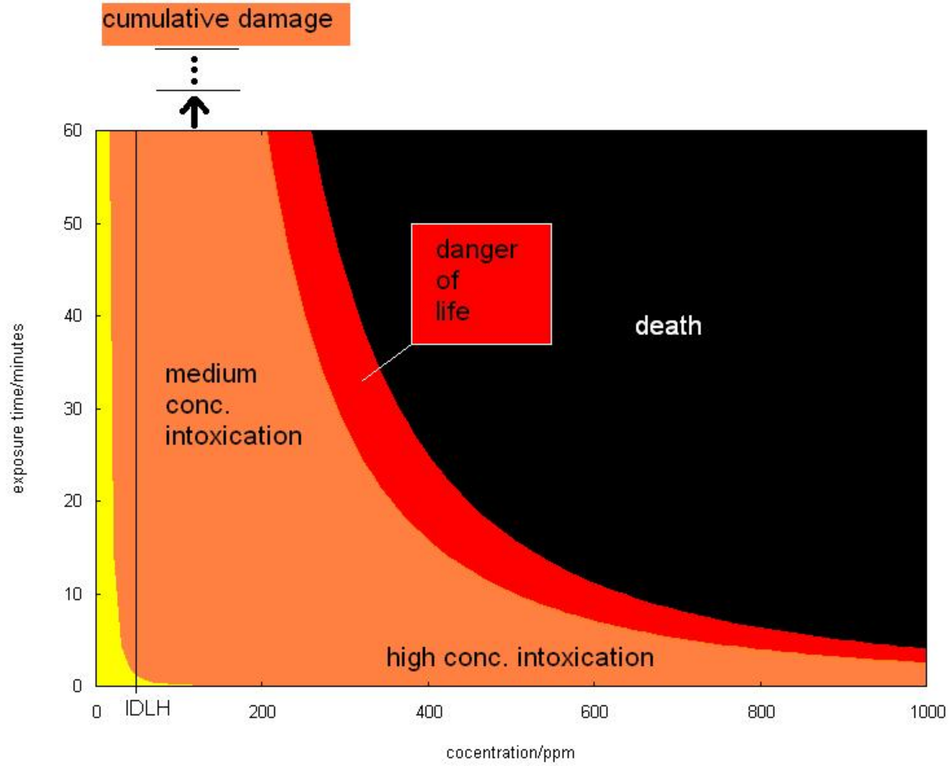
- white (crystaline) phosphorous is highly toxic (formed by P_4).
  → it disturbs severely the metabolism, especially the synthesis of proteins and hydrocarbons
  → white phosphorous is known to cause mutation of bones

- white phosphorous burns easily on air
- white phosphorous builts phosphoric acid (liquid) in humid environment.

Data partially from German Federal Institute for Occupational Safety and Health

Phosphorous Hydride (Phosphine) PH_3

- gaseous, resorbed through lungs
- medium concentrations cause headaches and drop of blood pressure plus cardiac arrhythmia
- high concentrations can cause cardiac defects and respiratory paralysis
- death usually occurs due to pulmonary edema (lungs malfunction)
- long exposure to low concentrations leads to dizziness, sickness, headache and icterus
- survivors retain damage of kidney and liver



IDLH – immediately dangerous to life and health (PH_3: IDLH = 50 ppm)

Data from German Federal Institute for Occupational Safety and Health

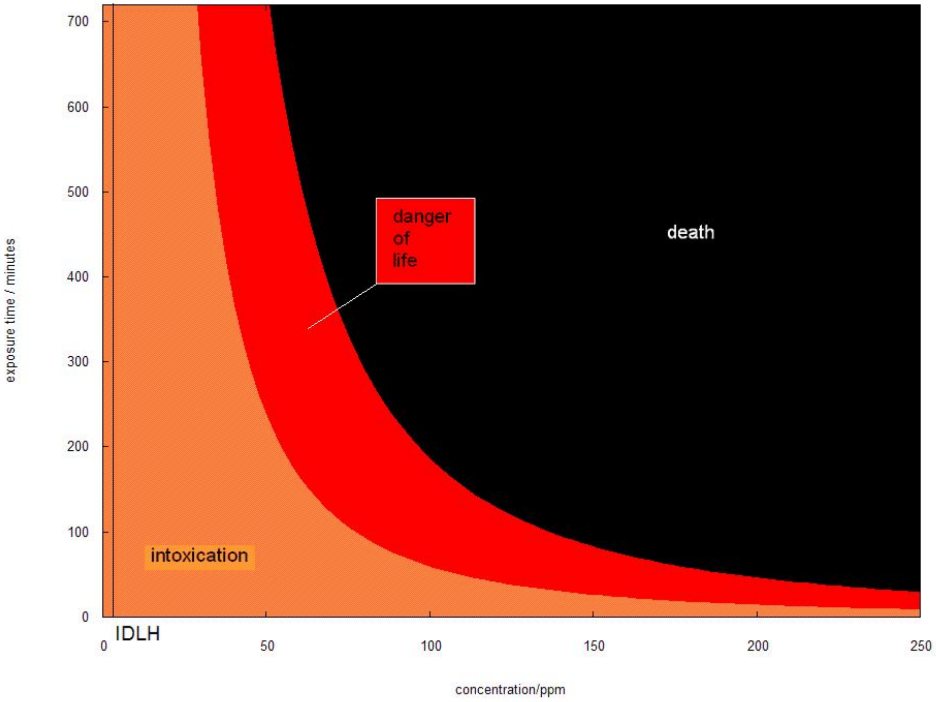
Arsenic (As)

- yellow As is highly toxic, but not a stable configuration
- due to its low solubility in water, elemental As is hardly resorbed
- intoxications are caused by arsenic ionic reaction products, mainly oxides - it heavily disturbs the digestive tract, the balance of electrolytes and the balance of water, leading to damage of organs, especially the kidneys
- chronic exposure damages the skin, diabetes and heart disease may also occur
- arsenic reaction products are genotoxic and have been proven to cause cancer

Data from German Federal Institute for Occupational Safety and Health

Arsenic Hydride (Arsine) AsH_3

- gaseous, resorbed through lungs
- causes hemolysis and kidney damage
- sickness appears within the first 24 hours of exposure
- heart, liver and spleen are also damaged
- death usually occurs due to heart failure
- survivors retain damage of their nerve system



(AsH_3: IDLH = 3 ppm)

Data from German Federal Institute for Occupational Safety and Health

Summary of the Occupational Exposure Limits (OEL)

	P	PH_3	P_2O_5	As	AsH_3	As/AsO_x
MAK / TWA	0.1 ppm 0.05 mg/m^3	0.1 ppm	--- 1 mg/m^3	--- 0.01 mg/m^3	0.05 ppm	--- 0.01 mg/m^3

TWA – time weighted average
MAK – Max. Arbeitsplatz-Konzentration
OEL – occupational exposure limits

TWA – the average concentration under which most people can work consistently 8 h without harmful effects (*ppm* – gases, vapours; *mg/m^3* – solids, particles)

Data from EC and the International Programme on Chemical Safety

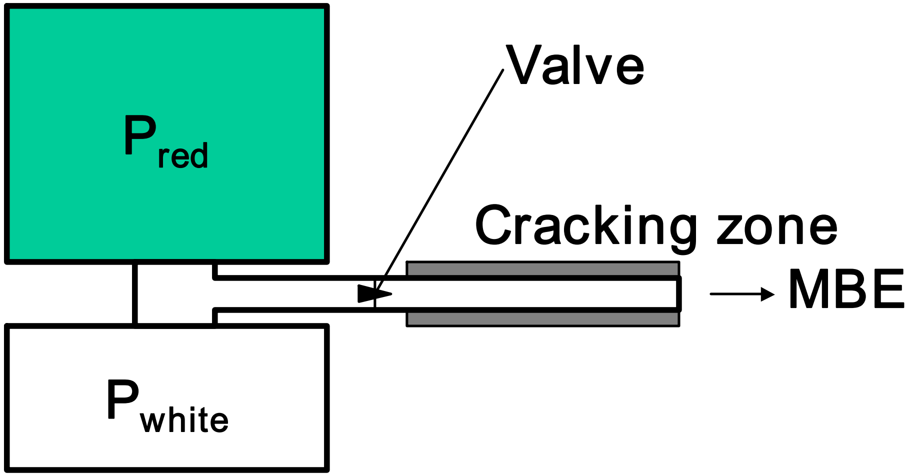
Molecular Beam Epitaxy: Modifications of Phosphorous

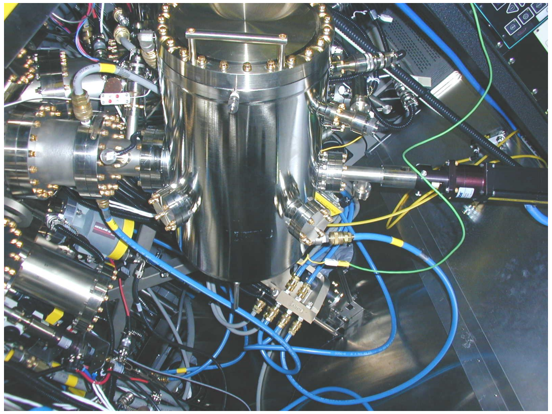
- Red Phosphorous:
  - amorphous
  - stable in air
  - burns at high temperature
  - evaporates as P_4

- White Phosphorous:
  - P_4 molecule
  - unstable in air (self inflammable)
  - high vapor pressure

Molecular Beam Epitaxy: Solid Source Phosphorous Cell

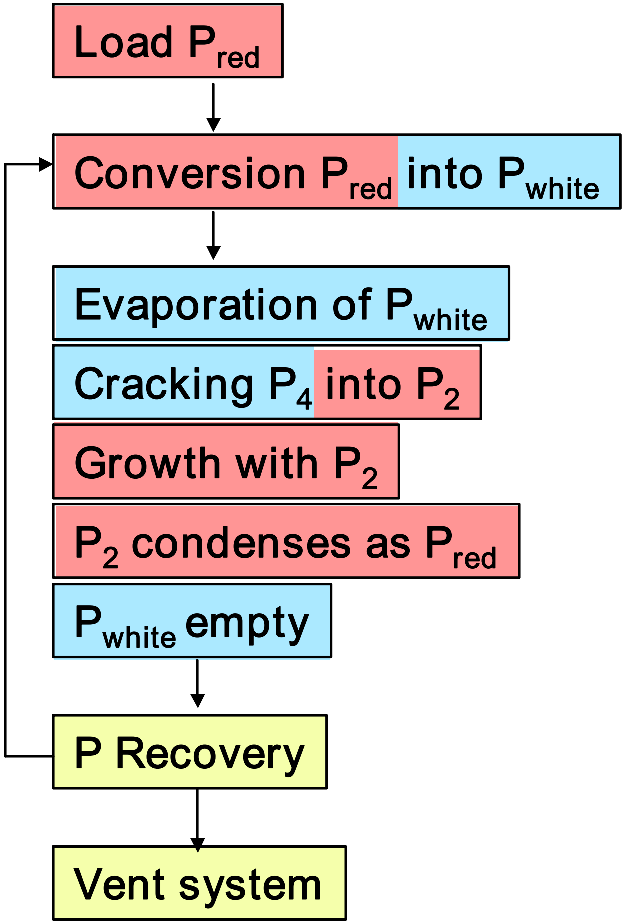
Three zone cracker cell





- Cracking efficiency < 100%
- P_{white} condenses on LN2 shroud
- P_{white} must be removed from system regularely

Operation Procedure



Load P_{red}

Conversion P_{red} into P_{white}

Evaporation of P_{white}

Cracking P_4 into P_2

Growth with P_2

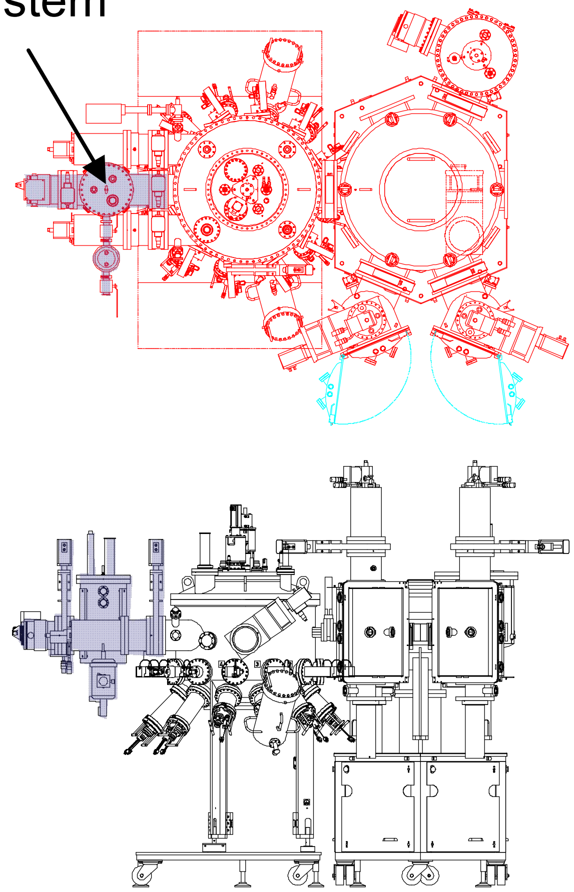
P_2 condenses as P_{red}

P_{white} empty

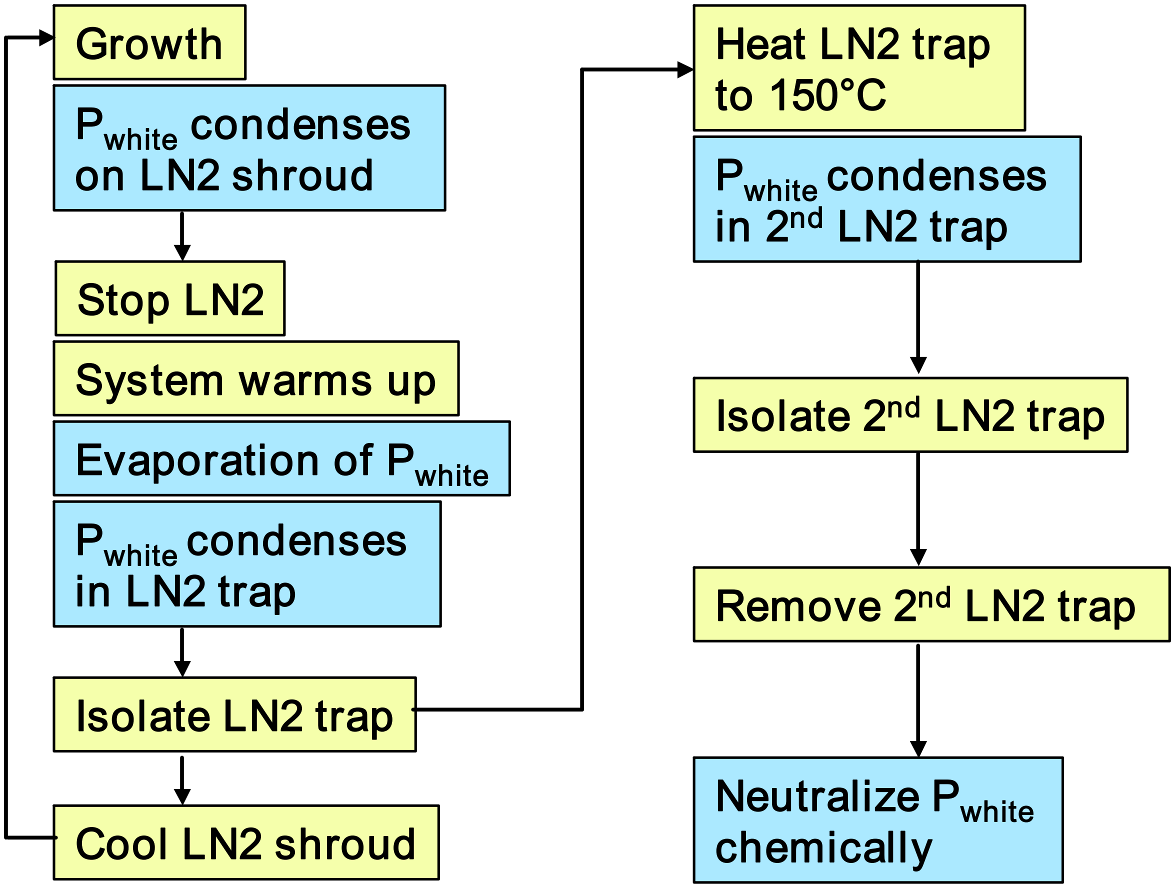
P Recovery

Vent system

Molecular Beam Epitaxy: Phosphorous Recovery



Phosphorous Recovery Procedure



Growth

P_{white} condenses on LN2 shroud

Stop LN2

System warms up

Evaporation of P_{white}

P_{white} condenses in LN2 trap

Isolate LN2 trap

Cool LN2 shroud

Heat LN2 trap to 150°C

P_{white} condenses in 2nd LN2 trap

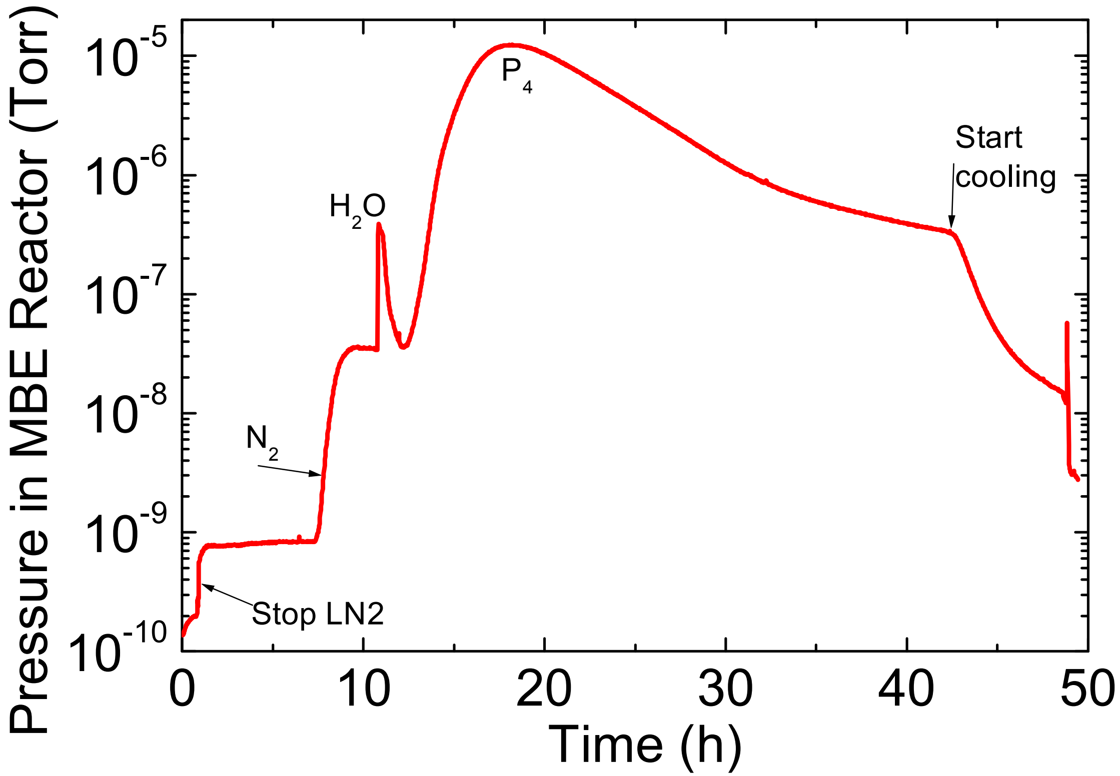
Isolate 2nd LN2 trap

Remove 2nd LN2 trap

Neutralize P_{white} chemically

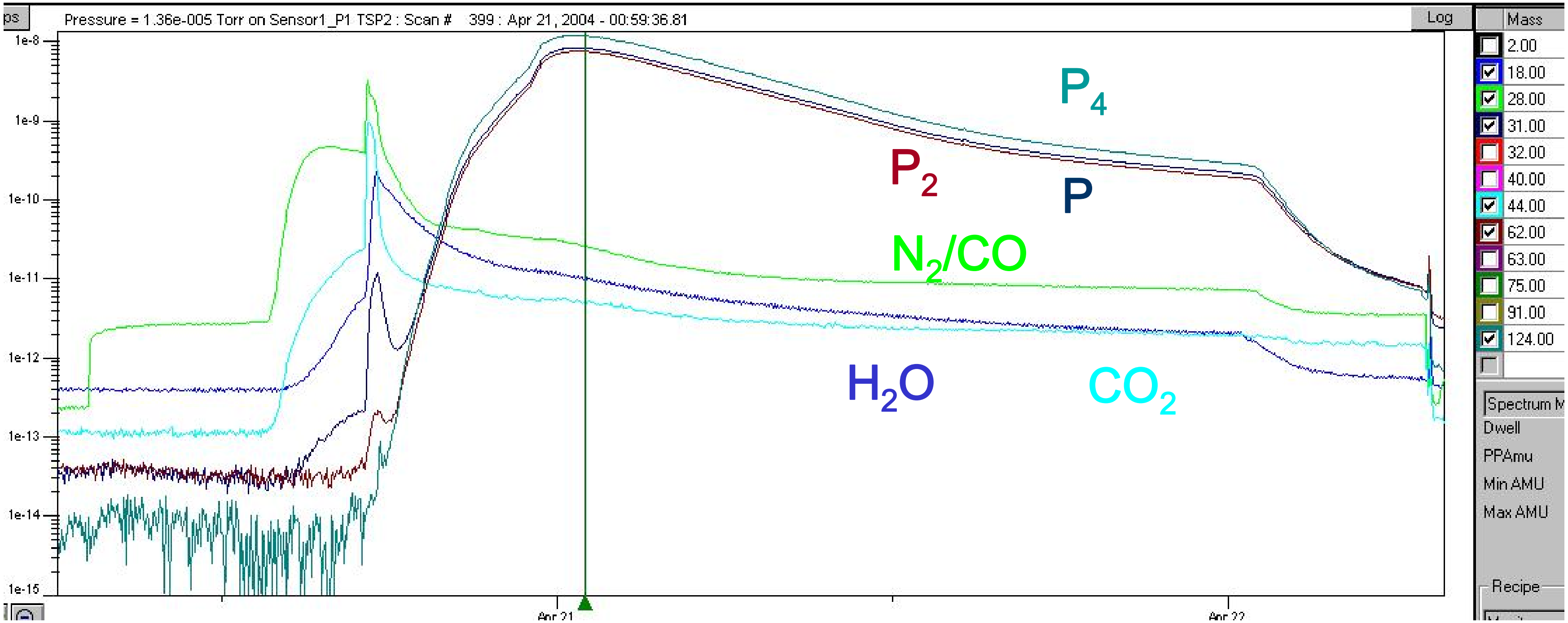
Molecular Beam Epitaxy: Phosphorous Recovery

Pressure inside MBE reactor during phosphorous recovery



Molecular Beam Epitaxy: Phosphorous Recovery

Mass spectrometric residual gas analysis inside MBE reactor during phosphorous recovery



Pressure = 1.36e-005 Torr on Sensor1_P1 TSP2 : Scan # 399 : Apr 21, 2004 - 00:59:36.81

Mass
☐ 2.00
☑ 18.00
☑ 28.00
☑ 31.00
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☐ 75.00
☐ 91.00
☑ 124.00
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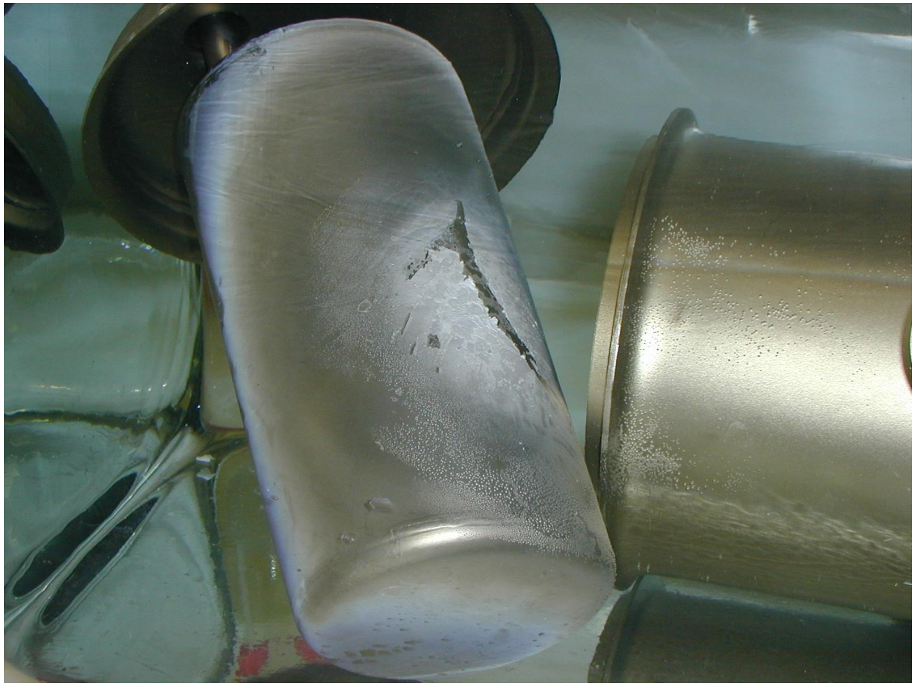
Molecular Beam Epitaxy: Phosphorous Recovery

Neutralization of P_{white}



$$P_4 + 5\ H_2O_2 + 12\ NH_4OH \rightarrow 4\ [PO_4(NH_4)_3] + 6\ H_2O + 5\ H_2$$

- After neutralization the end product can be safely handled

Molecular Beam Epitaxy: System maintenance

- Presence of As and P, as well as of their hydrides and oxides, must be considered
- Use of decontamination chemicals, which do not create toxic compounds of As and P
- Air sampling recommended
- Personal protection equipment
  - carrying of gas masks
  - using acid resistent gloves
  - be aware that also residual phosphorous can burn
    → for small openings fire might be stopped by immediate system closing
    → fire extinguisher recommended
- Training of the staff performing maintenance and handling of the MBE equipment

Summary

- Solid state molecular beam epitaxy is in comparison to other epitaxial equipment relatively safe. No danger at all during operation.

- However, one has to be careful during system maintenance
  → major concern is related on As and P treatment
  → most dangerous are related hydrides and oxides.

- Special treatment necessary with white phospourous
  → pyrolitic white phosphorous, acid formation, inflamable
  → safe phosphourous recovery process presented developed by IAF

- Safety recommendations for system maintenance:
  → Special training of staff needed
  → Individual protection equipment needed
  → Hydride sensoring recommended

Acknowledgement

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Thank you for your attention