Semiconductor silicon for microelectronics, power electronics and photonics, Russian scenerio

F.A. Kuznetsov

Institute of Inorganic chemistry, Siberian Branch of Russian academy of sciences

20th CODATA conference Beijing
24th October 2006

Semiconductor silicon – "hot" material of 21st century

Factors:

- Solar energy - demand already very high

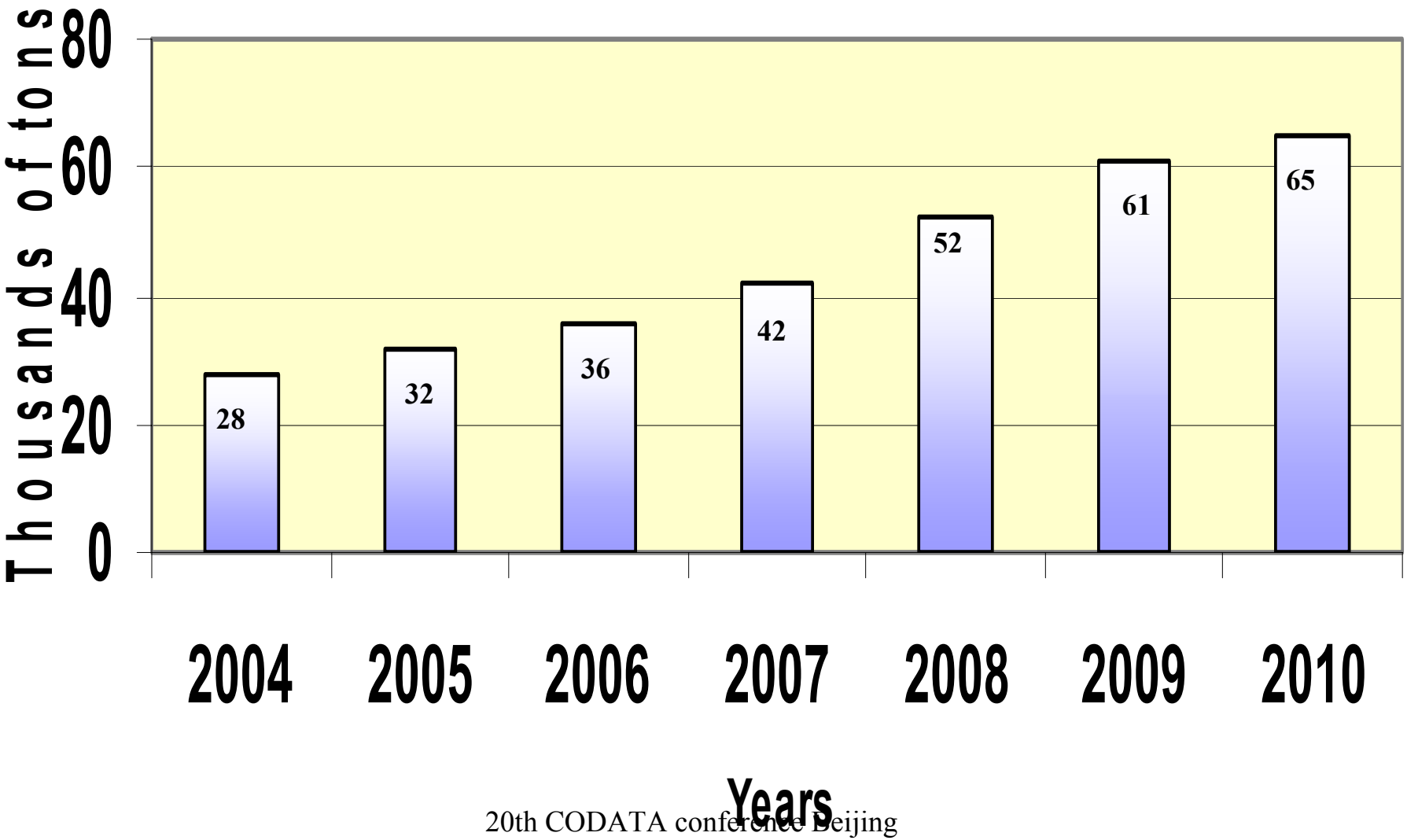
- Power electronics – significant growth of demand "around the corner"

Huge growth of energy needs in:

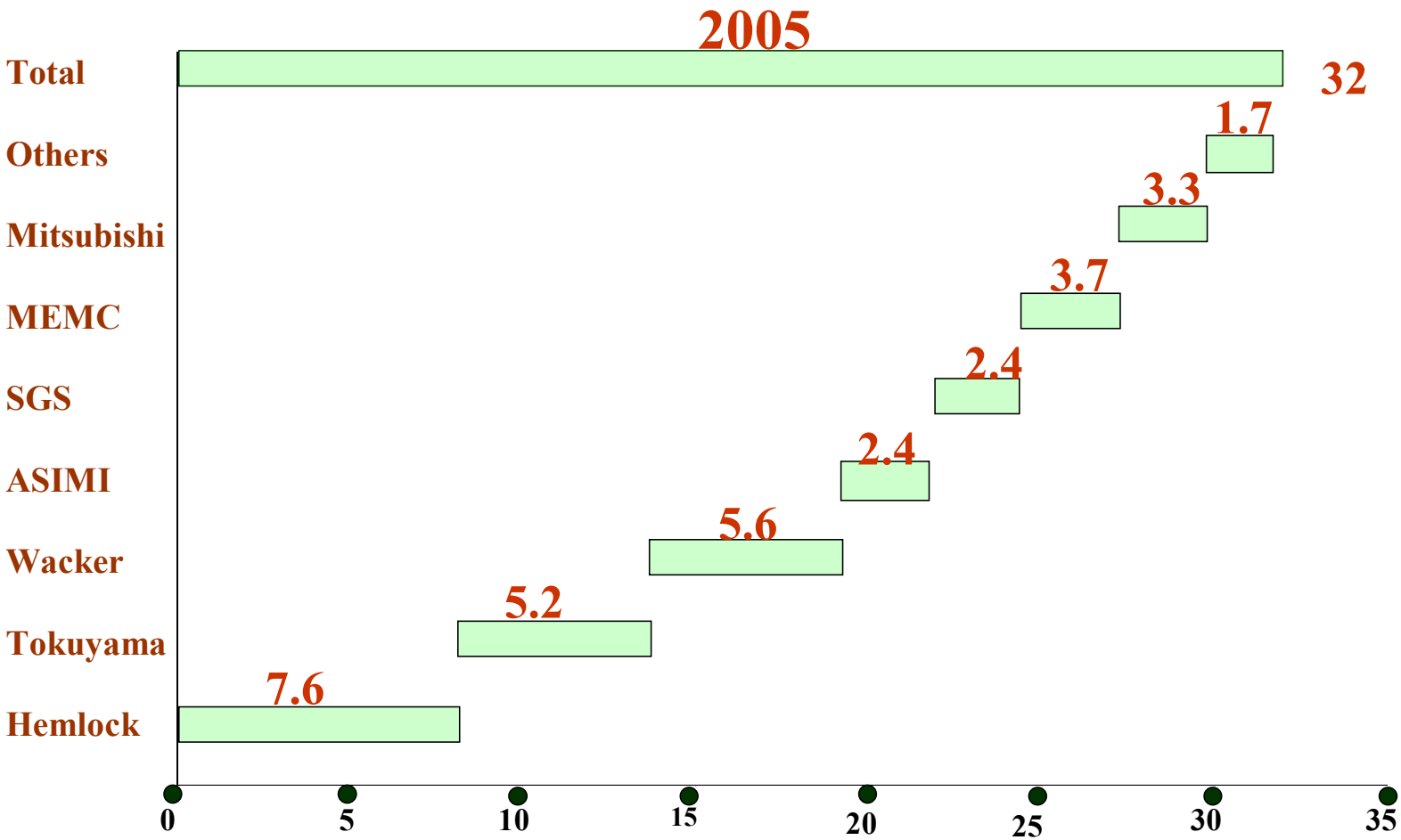
- China
- India
- Russia
- Brazil

……

Global Si production



Main world silicon producers



Amount of silicon produces. Mtonns

Problems of silicon supply

1. Decrease of production cost

2. Improving of material quality

3. Reduction of environmental load of production

What CODATA can do

Modeling of silicon technology processes as a way to:

- Shorten period of technology development

- Reduce cost of production

- Utilize dangerous waste products

Siemens process

Simplified processing

1. Synthesis of main reagent trichlorosilane

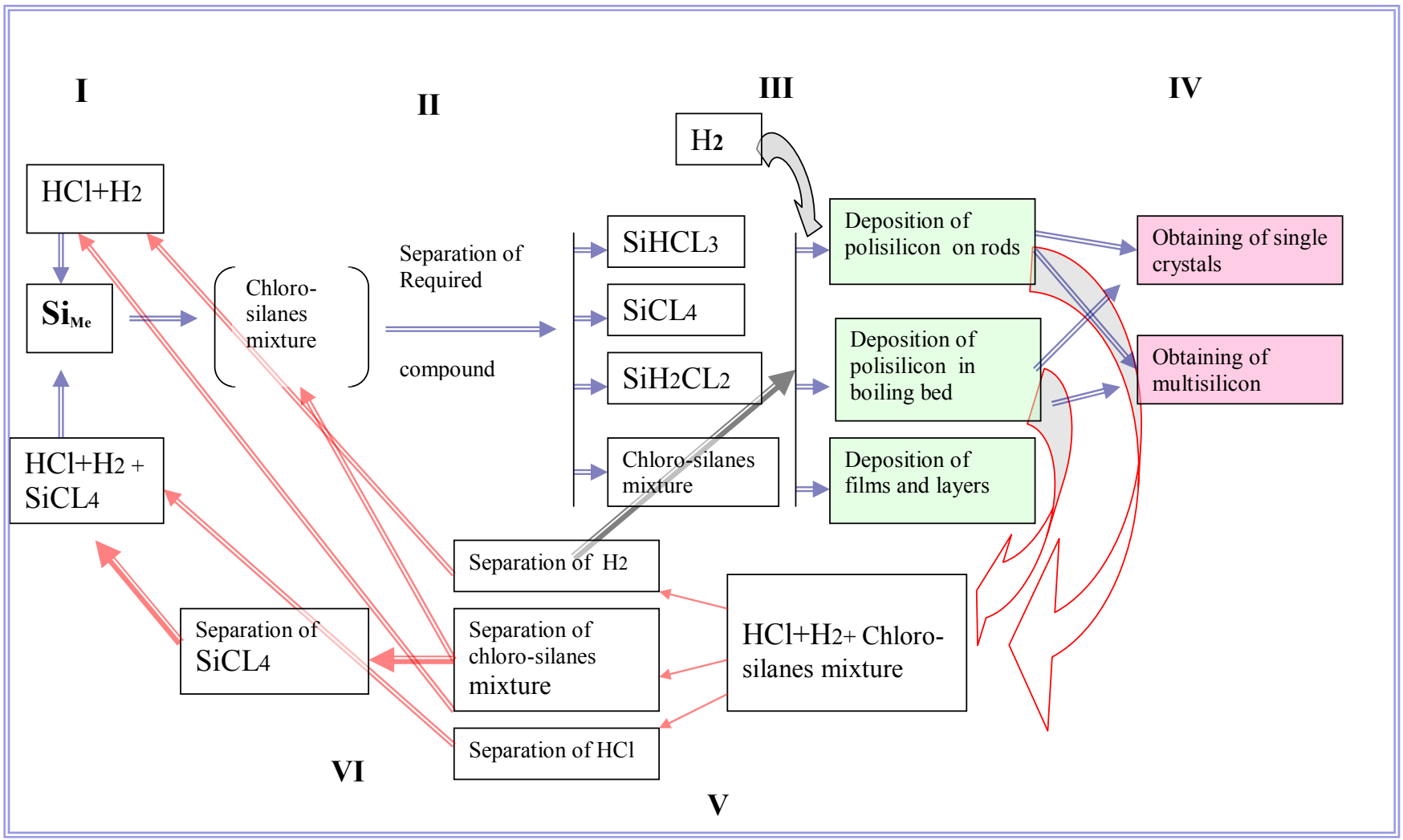
$$Si + HCl \longrightarrow SiHCl_3$$

2. Obtaining of poly silicon

$$SiHCl_3 + H_2 \longrightarrow Si + 3HCl$$

3. Growing of silicon single crystals

Main steps of Siemens process



The Si-H-Cl system

Gas species(21)**:**

Si, Si_2, Si_3, H, H_2, Cl, Cl_2, HCl, $SiCl$, $SiCl_2$, $SiCl_3$, $SiCl_4$, Si_2Cl_6, $SiHCl$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, SiH, SiH_2, SiH_3, SiH_4.

18 or 19 independent chemical reactions.

Thermodynamic functions for species:

$\Delta_f H^0$, S^0, $Cp = f(T)$;

$T = 25 - 1500^O$ C

$P = 0.5 - 10$ atm

	Gas phase in equilibrium (condensed phase can be obtained only from gas phase)	Condensed phase always presents	Energy stimulated reaction (condensed phase can be obtained only from gas phase)
1	$H_2=2H$	$H_2=2H$	$H_2=2H$
2	$SiCl_4=SiCl_3+Cl$	$SiCl_4=SiCl_3+Cl$	$SiCl_4=SiCl_3+Cl$
3	$2Cl=Cl_2$	$2Cl=Cl_2$	$2Cl=Cl_2$
4	$H+Cl=HCl$	$H+Cl=HCl$	$H+Cl=HCl$
5	$SiCl_4=SiCl_2+Cl_2$	$SiCl_4=SiCl_2+Cl_2$	$SiCl_4=SiCl_2+Cl_2$
6	$SiCl_3=SiCl+Cl_2$	$SiCl_3=SiCl+Cl_2$	$SiCl_3=SiCl+Cl_2$
7	$SiCl=Si+Cl$	$SiCl=Si+Cl$	$SiCl=Si+Cl$
8	$Si+H=SiH$	$Si+H=SiH$	$Si+H=SiH$
9	$Si+H_2=SiH_2$	$Si+H_2=SiH_2$	$Si+H_2=SiH_2$
10	$SiH+H_2=SiH_3$	$SiH+H_2=SiH_3$	$SiH+H_2=SiH_3$
11	$SiH_2+H_2=SiH_4$	$SiH_2+H_2=SiH_4$	$SiH_2+H_2=SiH_4$
12	$SiH+Cl=SiHCl$	$SiH+CL=SiHCl$	$SiH+CL=SiHCl$
13	$SiHCl+H_2=SiH_3Cl$	$SiHCl+H_2=SiH_3Cl$	$SiHCl+H_2=SiH_3Cl$
14	$SiH_2+Cl_2=SiH_2Cl_2$	$SiH_2+Cl_2=SiH_2Cl_2$	$SiH_2+Cl_2=SiH_2Cl_2$
15	$SiHCl+Cl_2=SiHCl_3$	$SiHCl+Cl_2=SiHCl_3$	$SiHCl+Cl_2=SiHCl_3$
16	$2Si=Si_2$	$2Si=Si_2$	$2Si=Si_2$
17	$3Si=Si_3$	$3Si=Si_3$	$3Si=Si_3$
18	$2SiCl_3=Si_2Cl_6$	$2SiCl_3=Si_2Cl_6$	$2SiCl_3=Si_2Cl_6$
19	$P_{si}^{*}=RT\Sigma\alpha_{I,Si}n/V=$ $=\Sigma\alpha_{I,Si}n*P_I$	$Si=Si(cr)$	$P_{Si}=\exp(\partial E/\partial n_{Si}-\mu_{Si}^{0})$
20	$P_H^{*}=\alpha_{I,H}*P_I$	$P_H^{*}=\alpha_{I,H}*P_I$	$P_H^{*}=\alpha_{I,H}*P_I$
21	$P_{Cl}^{*}=\Sigma\alpha_{I,Cl}*P_I$	$P_{Cl}^{*}=\Sigma\alpha_{I,Cl}*P_I$	$P_{Cl}^{*}=\Sigma\alpha_{I,Cl}*P_I$

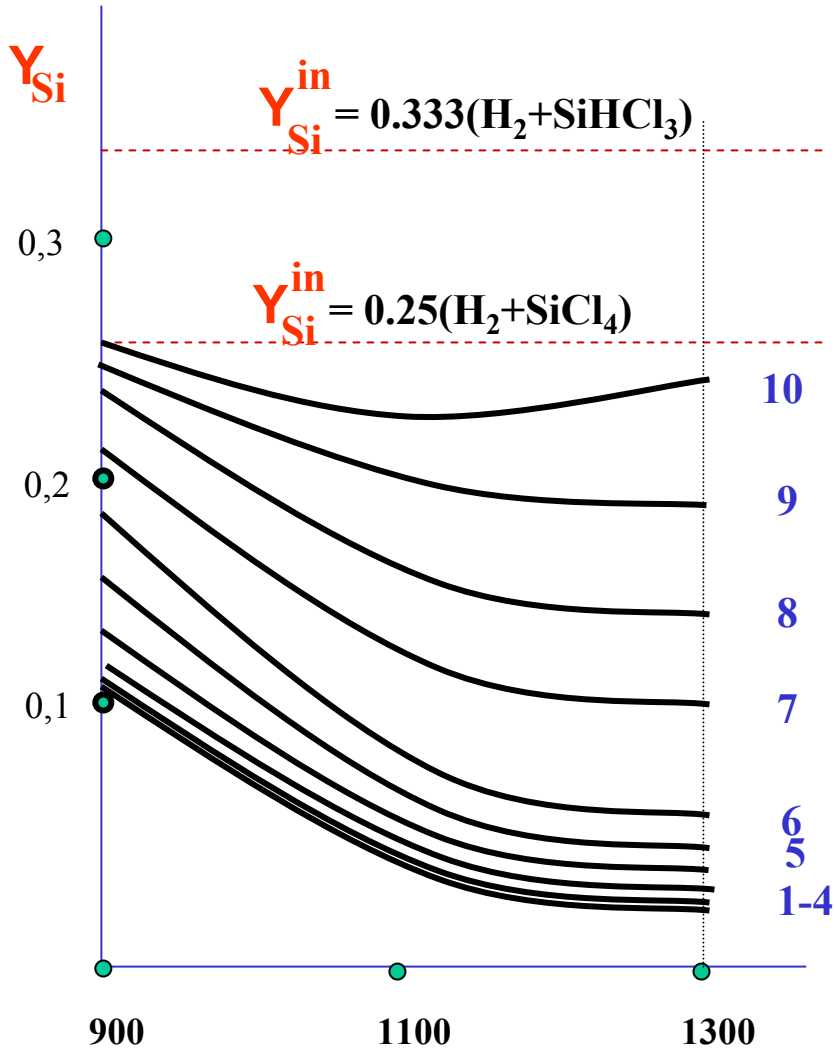
Values obtained by calculation

1. Partial pressures of gas species P_i
2. Relative solubility of silicon

$$Y_{Si} = n_{Si} / n_{cl} = \Sigma\, k_{Si} P_i \,/ \Sigma\, k_{cl} P_i$$

3. Yeald of silicon

$$\frac{(Y_{si})_{in} - (Y_{si})_{eq}}{(Y_{si})_{in}}$$



$$Y_{Si} = \frac{n_{Si}}{n_{Cl}}$$

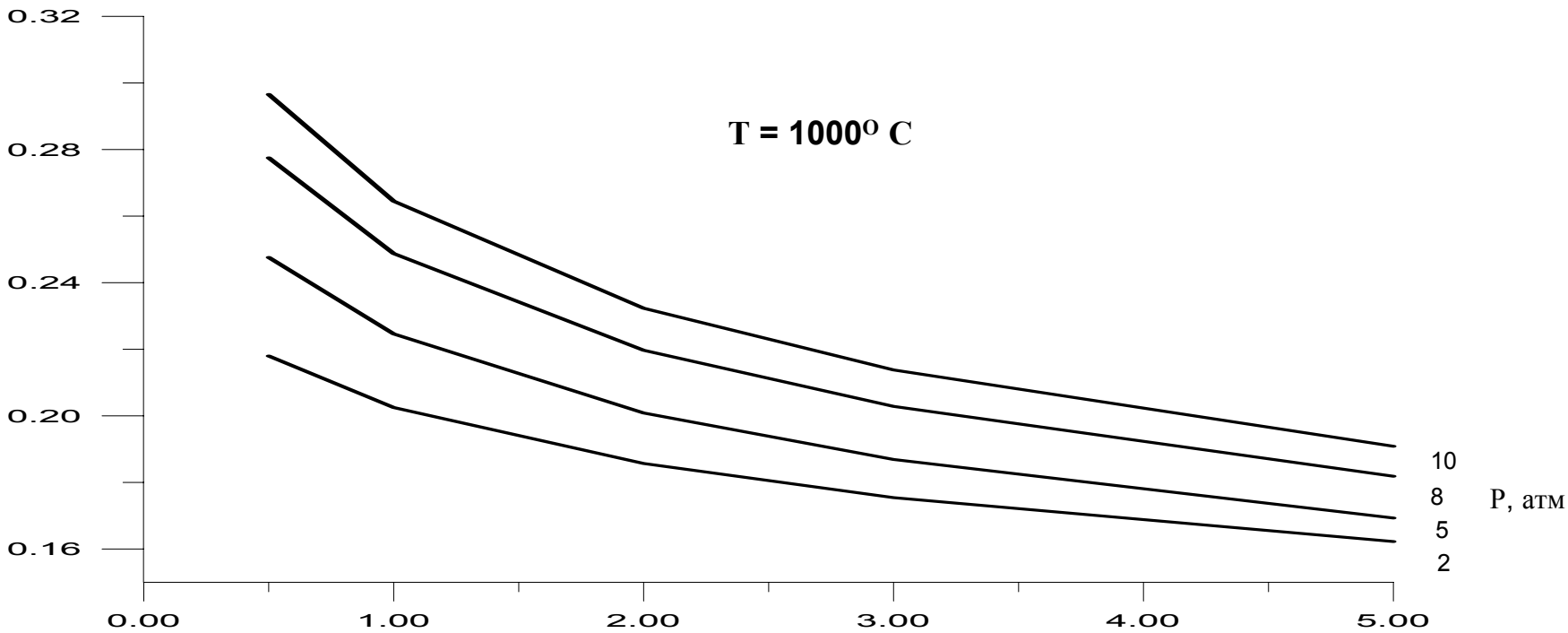
$$Q = \frac{n_{Cl}}{n_H}$$

Values of Q:

1 - 0,001;	6- 0,032
2 - 0,002;	7 - 0,064
3 - 0,004	8 – 0,128
4 - 0,008	9 – 0,256
5 - 0,016	10 – 0,512

Reduction of $SiHCl_3$

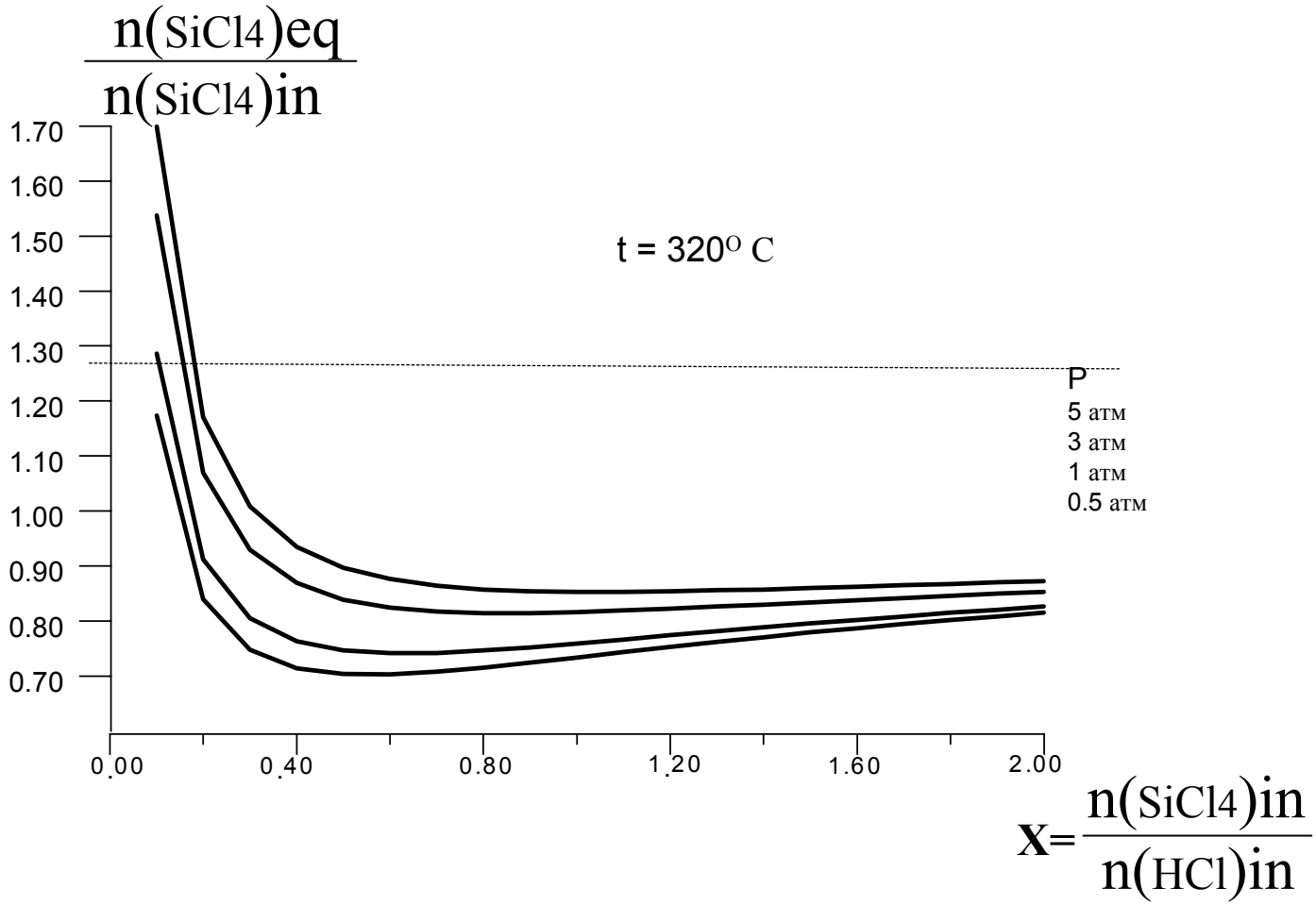
$$\frac{(n_{Si})_{sol}}{n_{(SiHCl_3)in}}$$



$$\frac{n_{(H2)in}}{n_{(SiHCl_3)in}}$$

Pressure dependence of silicon yield

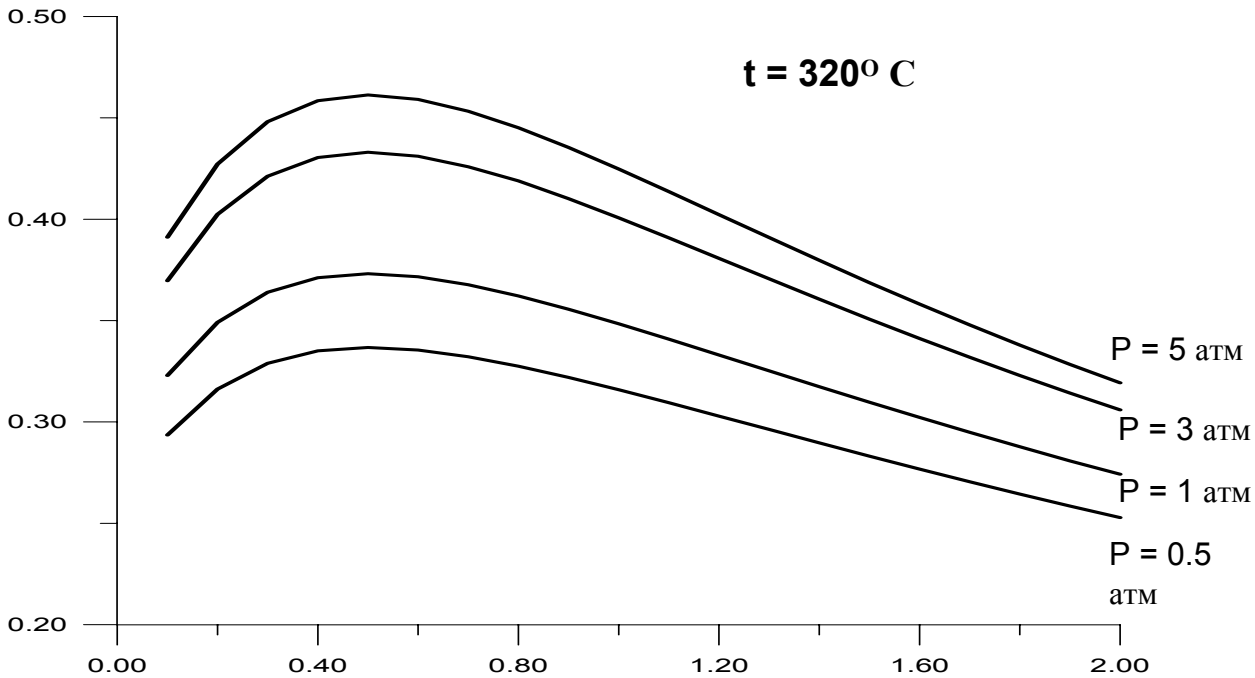
Dissolving of metallurgical silicon



Conversion of $SiCl_4$ in reactor for $Si_{(Me)}$ etching

Dissolving of metallurgical silicon

$$\frac{n(SiHCl3)\ eq}{n(HCL)in+n(SiCl4)in}$$

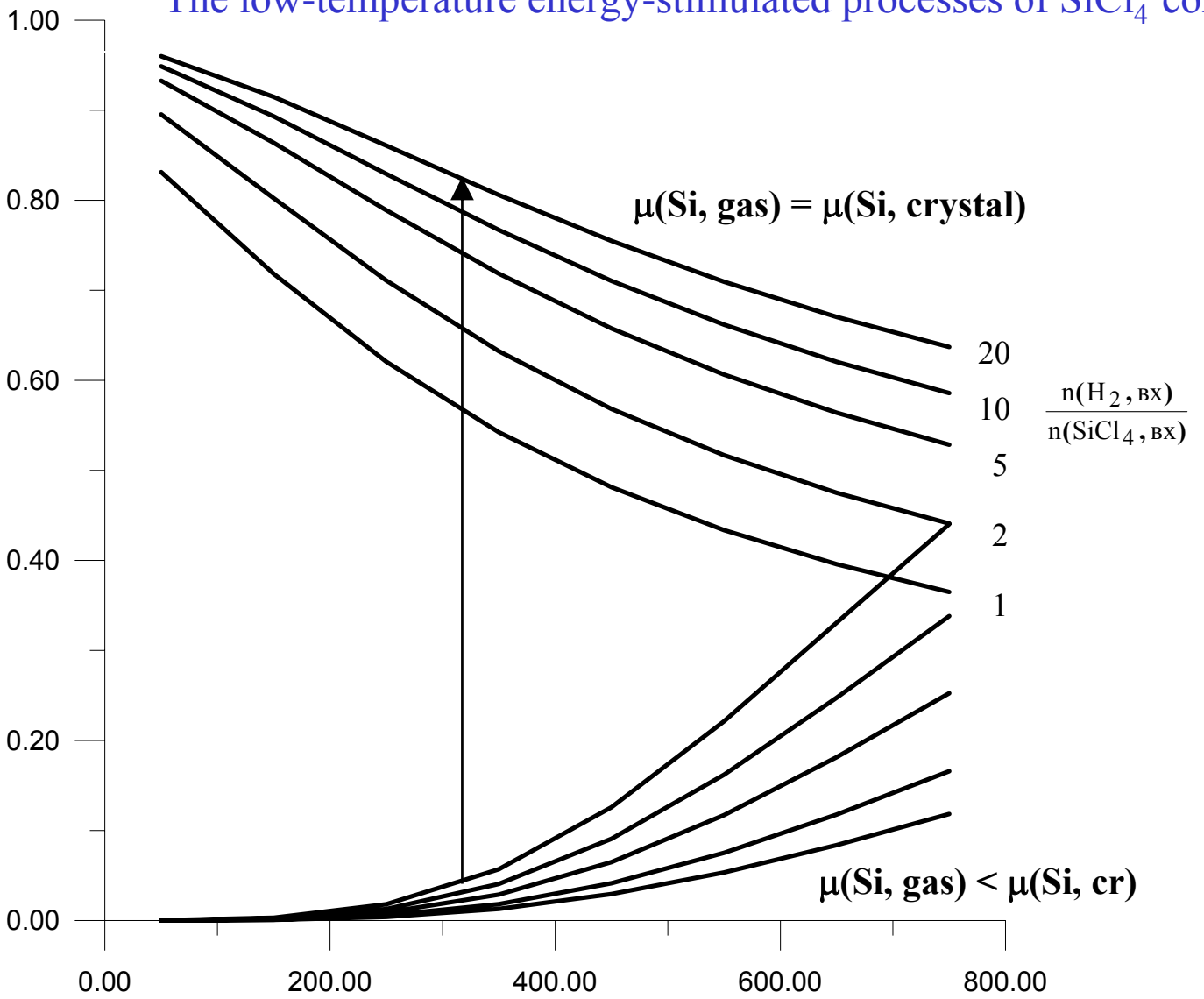


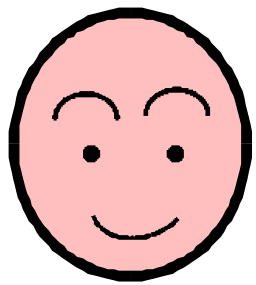
$$X=\frac{n(SiCl4)in}{n(HCl)in}$$

Productivity of reactor for synthesis of $SiHCl_3$

Grows of $SiHCl_3$ yield under forced increasing of μ(Si, gas)

The low-temperature energy-stimulated processes of $SiCl_4$ conversion





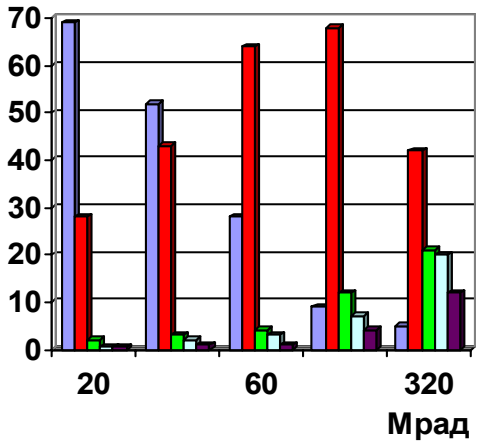
Conversion of $SiCl_4$ under electron beam

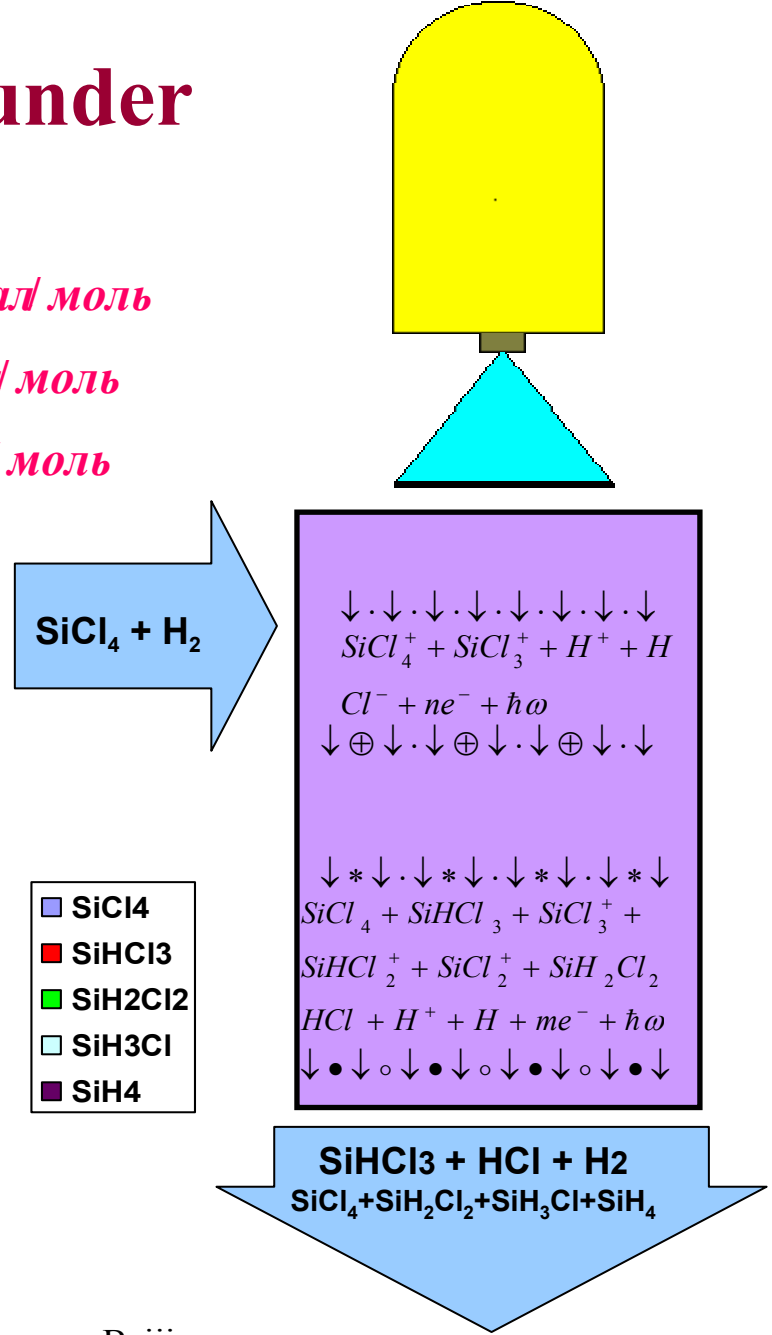
$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl, \ldots \Delta H^\circ = 16{,}5 \text{Ккал/моль}$$

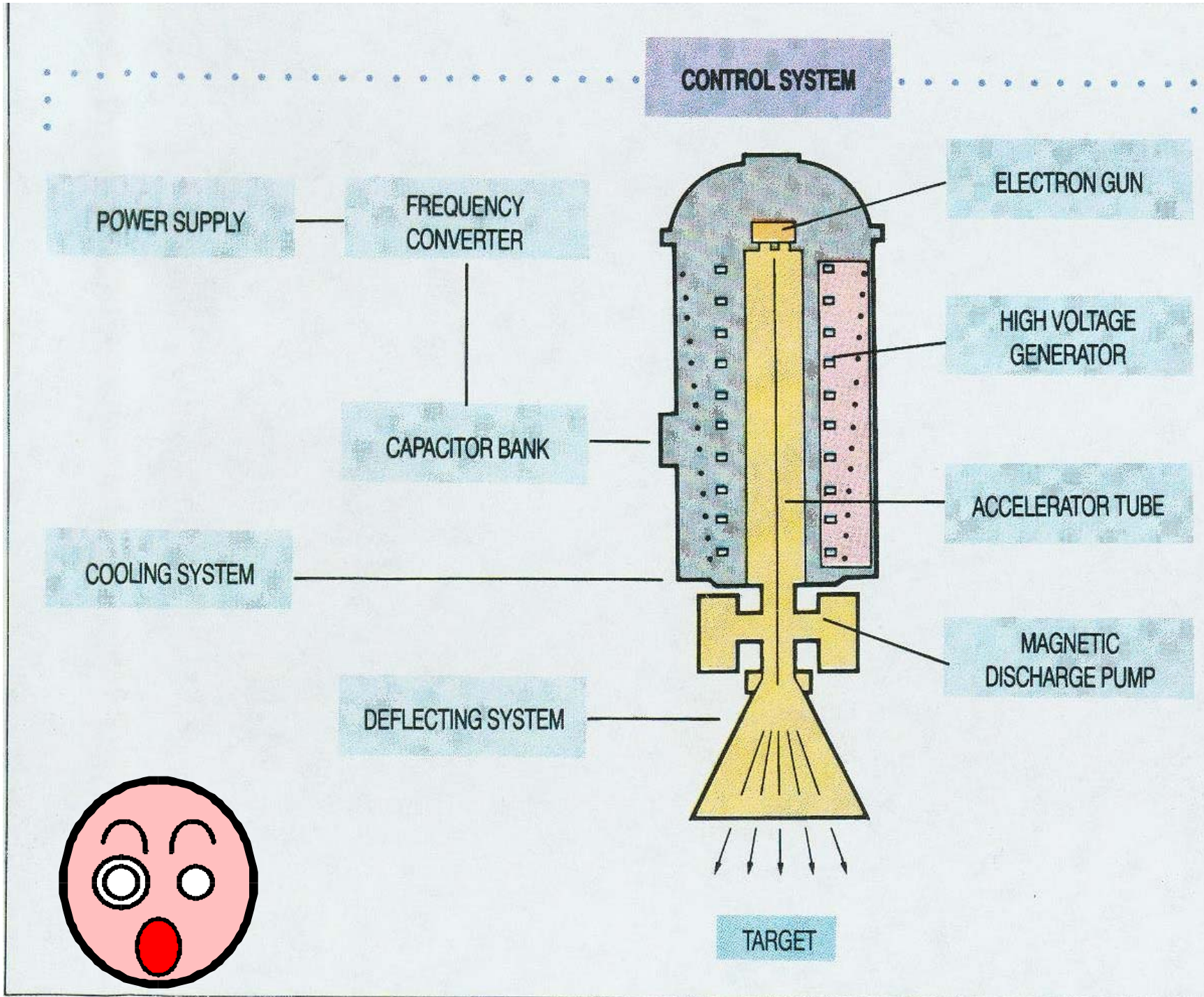
$$SiCl_4 \rightarrow SiCl_3 + Cl, \ldots\ldots\ldots\ldots \Delta H^\circ = 111 \text{Ккал/моль}$$

$$H_2 \rightarrow H + H, \ldots\ldots\ldots\ldots\ldots\ldots \Delta H^\circ = 105 \text{Ккал/моль}$$

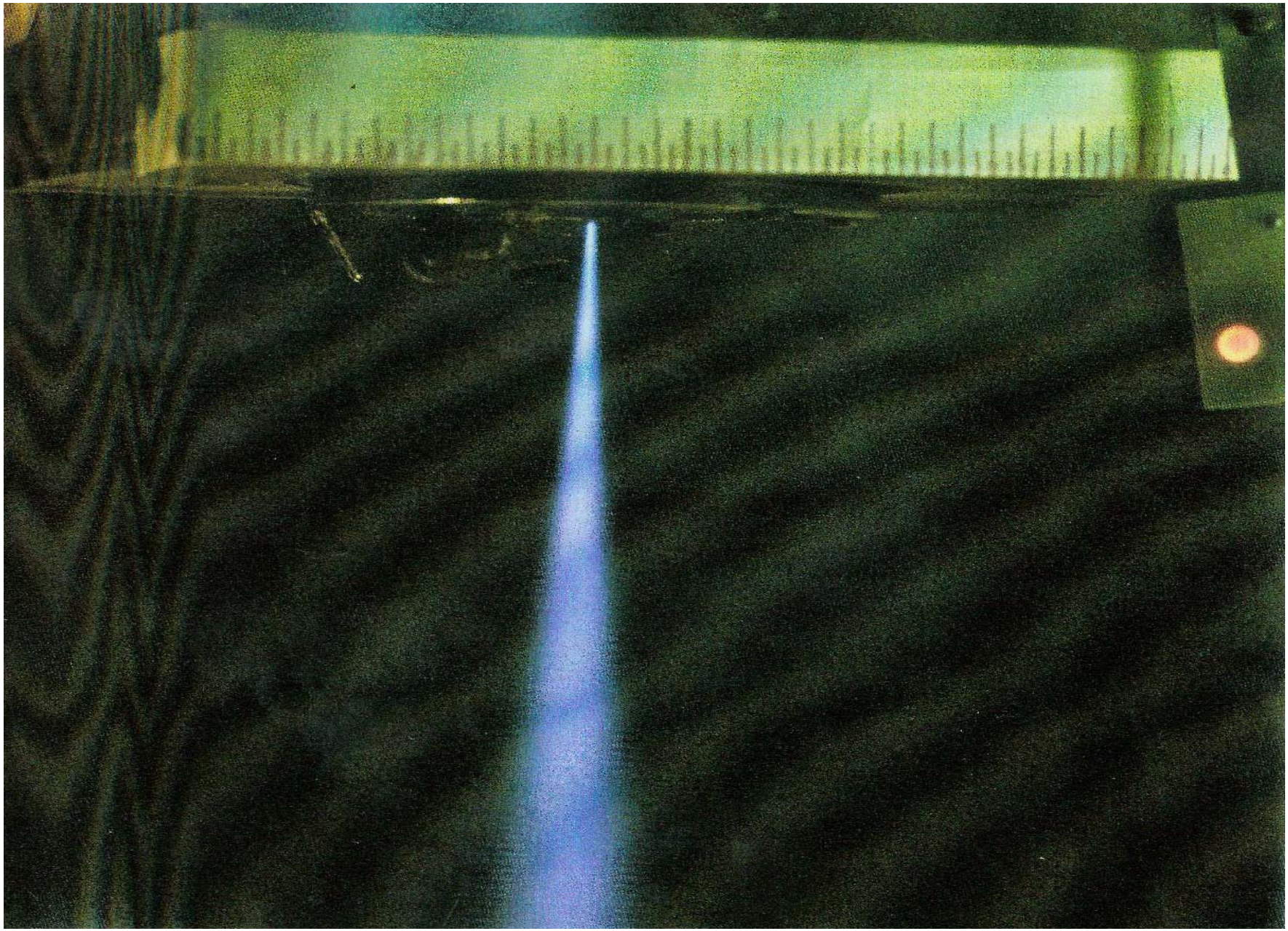
Content of different hydrochlorides in reaction products as a function of irradiation dose.
(10 M rad= 4,1 Kcal/mol)






CONTROL SYSTEM
POWER SUPPLY
FREQUENCY CONVERTER
ELECTRON GUN
HIGH VOLTAGE GENERATOR
CAPACITOR BANK
ACCELERATOR TUBE
COOLING SYSTEM
MAGNETIC DISCHARGE PUMP
DEFLECTING SYSTEM
TARGET

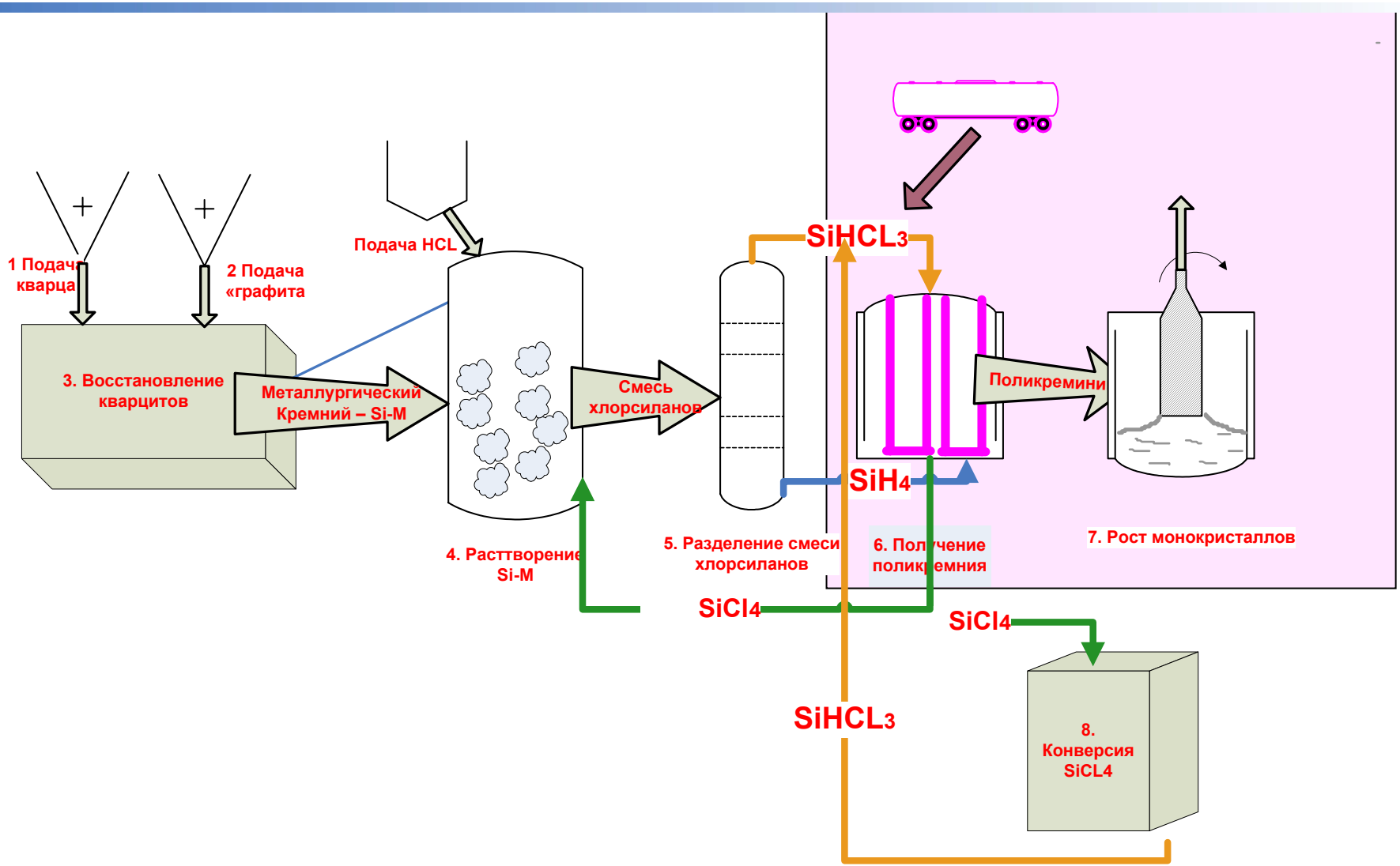
E-beam



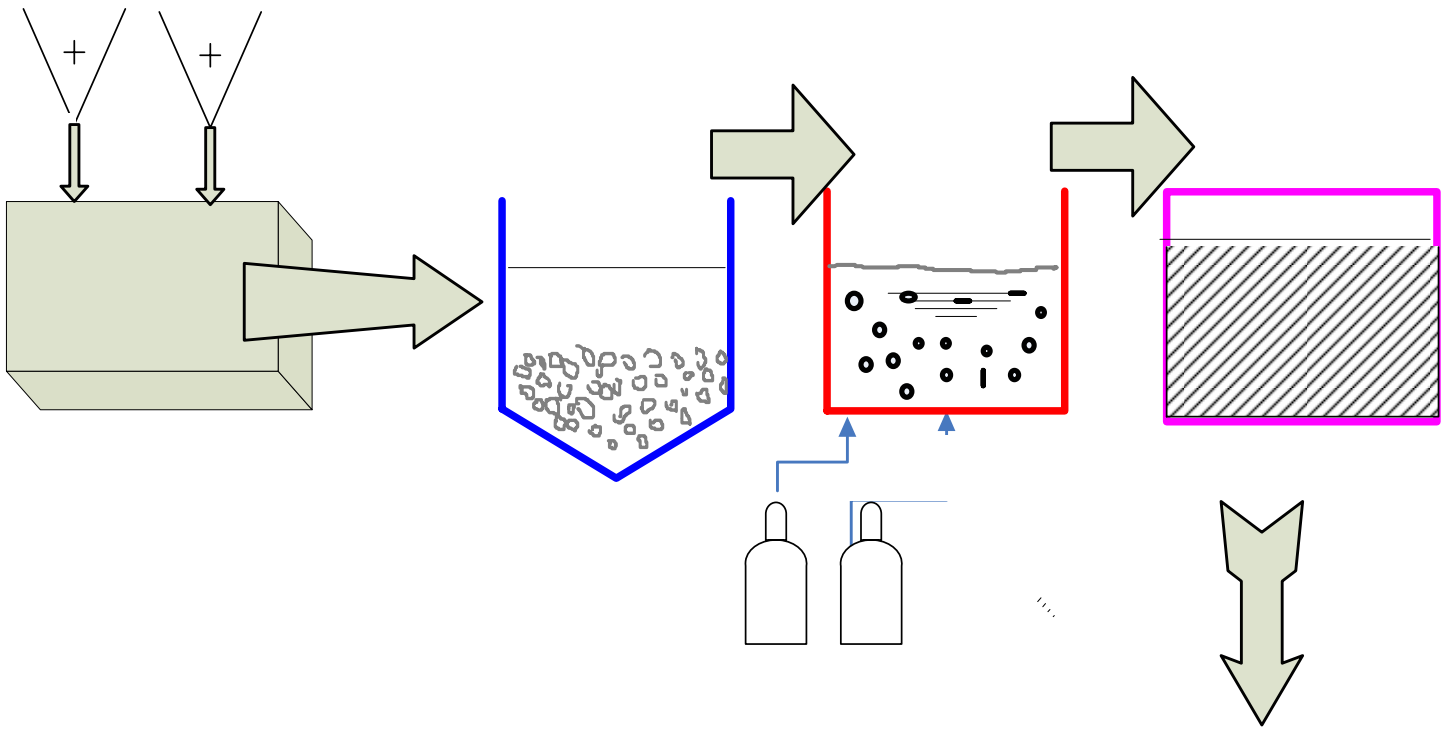
Used and potential processes for poly silicon production

20th CODATA conference Beijing
24th October 2006

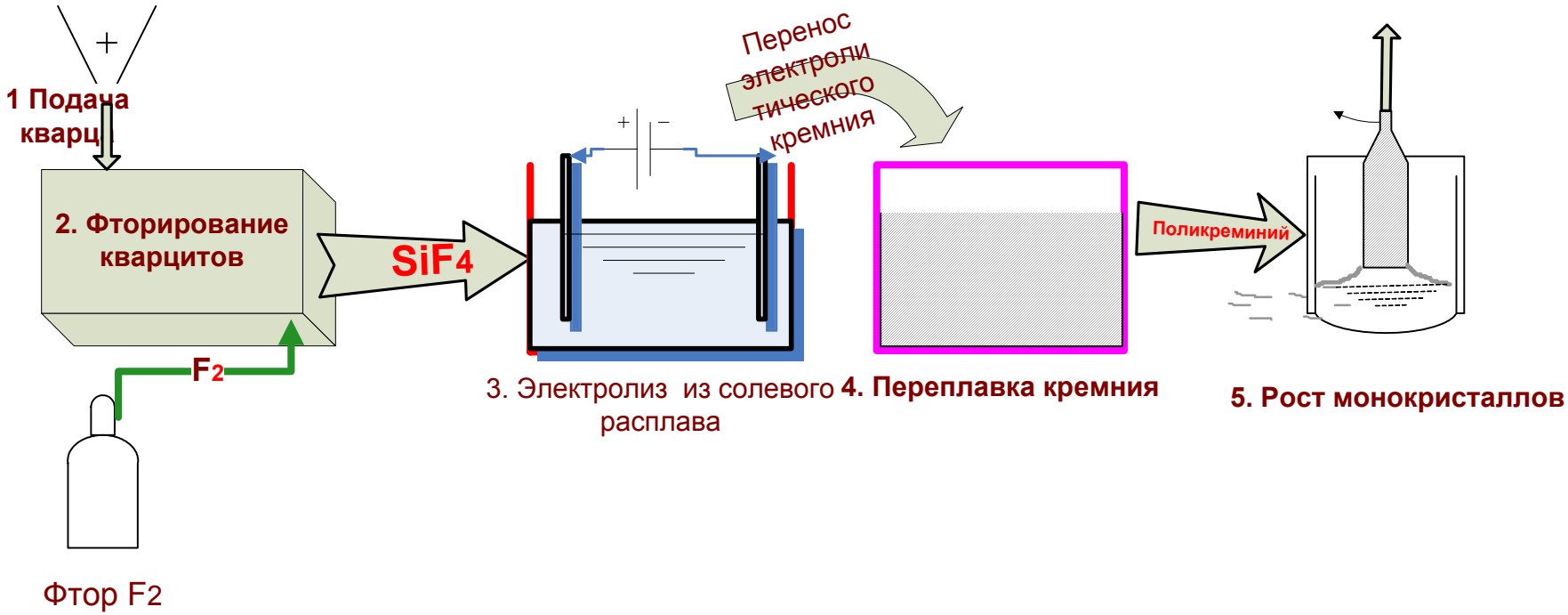
Хлоридный (Сименс) процесс



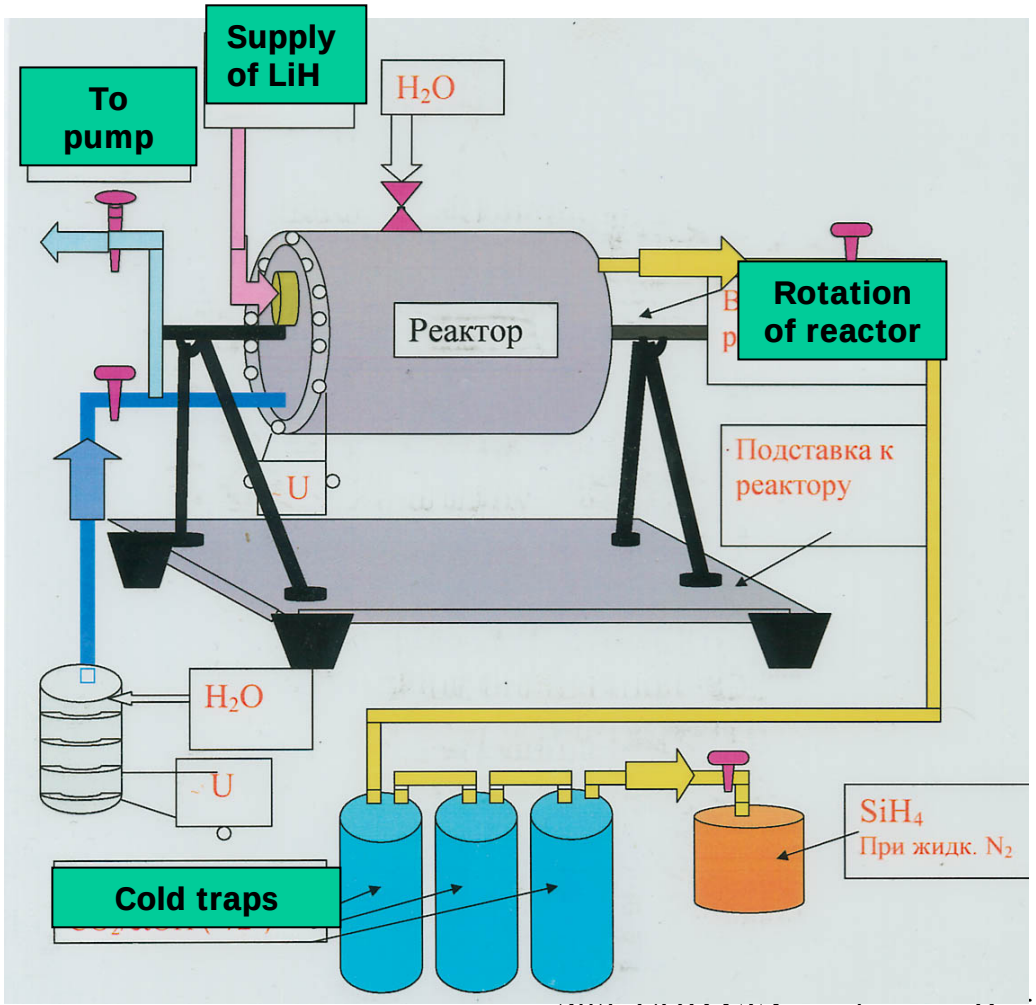
Carbothermal process



Fluoride process



Production of monosilane with use of LiH



Scheme of a set up for receiving of SiH_4 by interaction of Li_4Si with water vapor

Production of monosilane with use of LiH

$$SiCl_4 + LiH \longrightarrow SiH_4 + LiCl$$

$$SiO_2 + LiH \xrightarrow{840^oC} Li_4Si + Li_xSi_y + H_2O$$

$$Li_4Si + H_2O_{solid} \longrightarrow SiH_4 + Li_2O + Li_2SiO_3 + LiOH$$

Advantages of the proposed method are:

- Outcome of monosilane can rich 80%
- Carbon impurity content can be reduced
- Overall purity of monosilane can be enhanced

Production of monosilane with use of LiH

$$SiO_2 + LiH \xrightarrow{840^oC} Li_4Si + Li_xSi_y + H_2O\uparrow$$

Interaction of lithium silicides with ice

$$Li_4Si + H_2O_s \longrightarrow SiH_4\uparrow + Li_2O + Li_2SiO_3 + LiOH$$

Yield of monoclines is 50 % or more

In case of interaction of Li_4Si with 10% HCl at temperature - 74.7oC monosilane yield reaches 80%

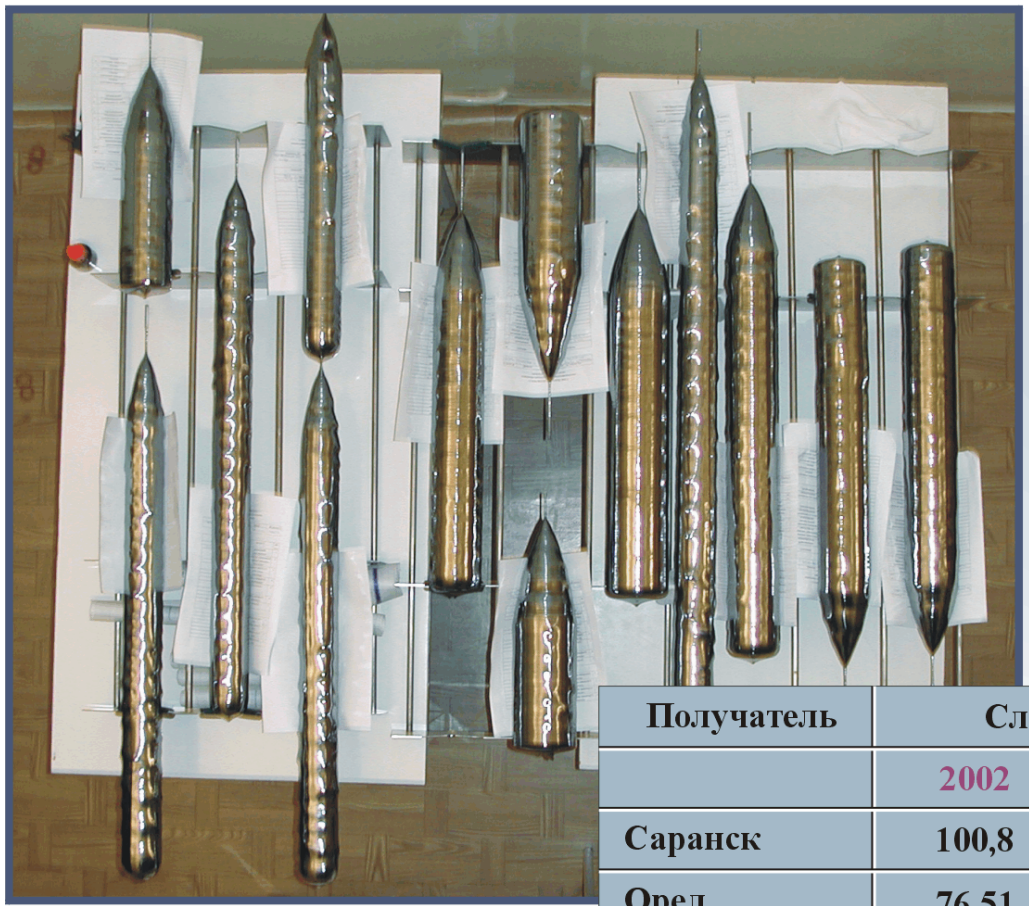
Cz Silicon of KMCC

Conclusions

1. Semiconductor silicon is and for a long time will be one of most critical materials of technical progress.

2. Demands for silicon contentiously grow, technical requirements become more severe. So, silicon technology is an example of science intensive processing

3. Modeling in silicon technology with use of reliable data is a way to meet growing demands for quantity and quality of silicon for different applications.

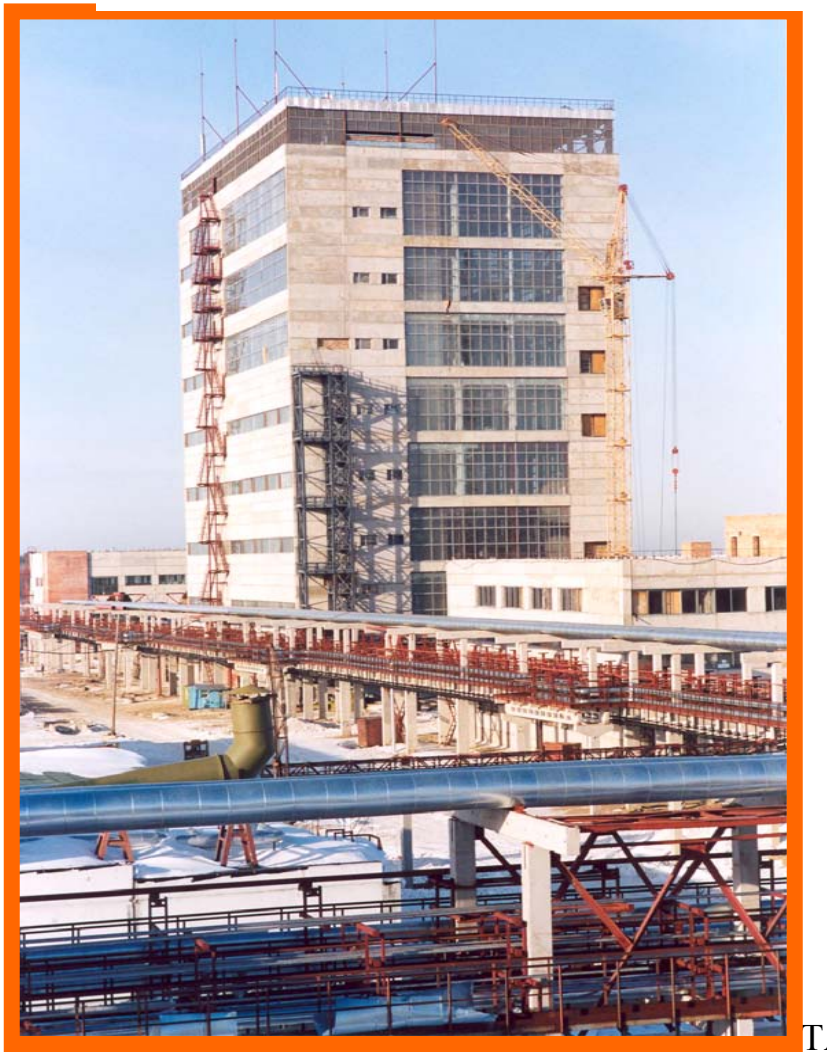


FZ silicon

Поставки БЗП кремния

Получатель	Слитки (кг.)		Пластины и структуры (шт.)	
	2002	2003	2002	2003
Саранск	100,8	109,9		
Орел	76,51	53,5		
Прочие	5,2	3,2	50	15
Новосибирск			180	50

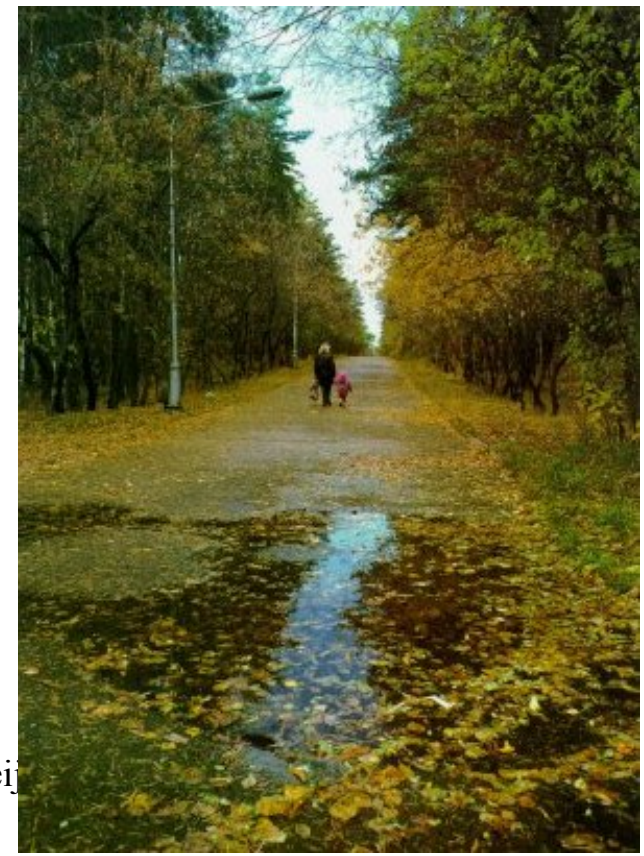
Semiconductor silicon plant Zheleznogorsk city, Siberia



- **Planned production capacity of constructions 1.2-2.0 thousand tons**
- **Project – institute GIREDMET, technology scheme and optimal regimes developed at active participation of NIICh SB RAS**

Zheleznogorsk city

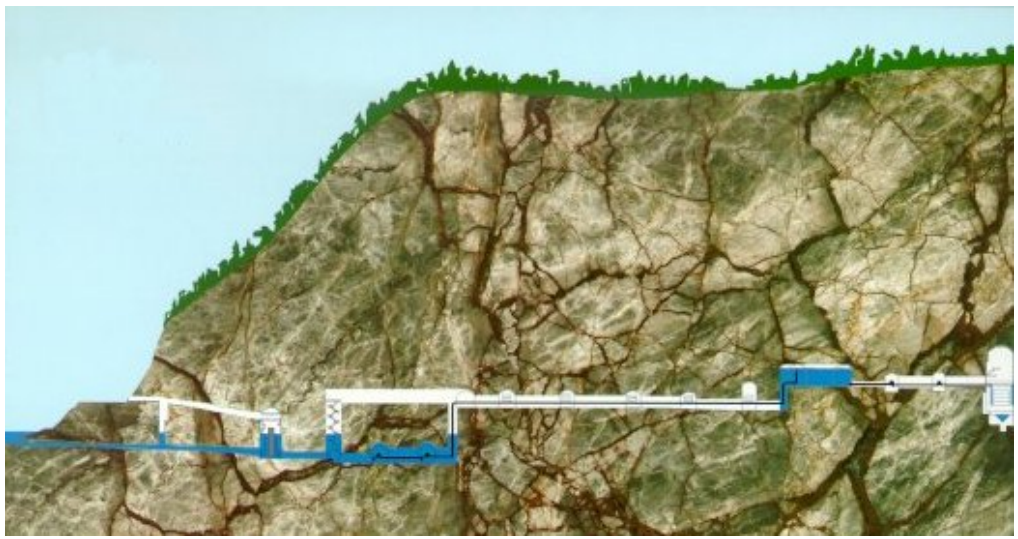
Was started in 1950. Received officially its name in 1994. Population 100 000, territory 17.1 sq.km



Krasnoyarsk – 26

Enisei river

View of tunnel



Water supply for cooling of reactors

Workspace inside mountains

Model of RT-2

Construction site of RT-2

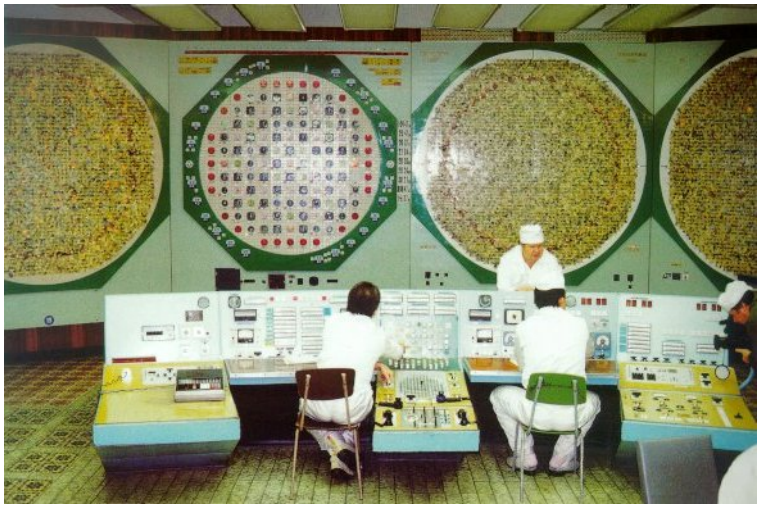
Spent fuel storage

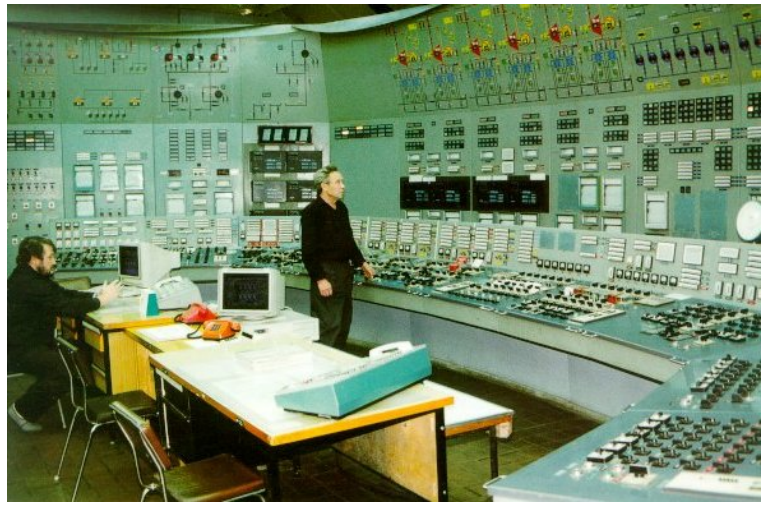
Special rail road car

RT-2,
Zheleznogorsk

Assemblies in water storage

Krasnoyarsk – 26





Reactor and turbines control halls

Turbines and generators hall

Neutrino research laboratory

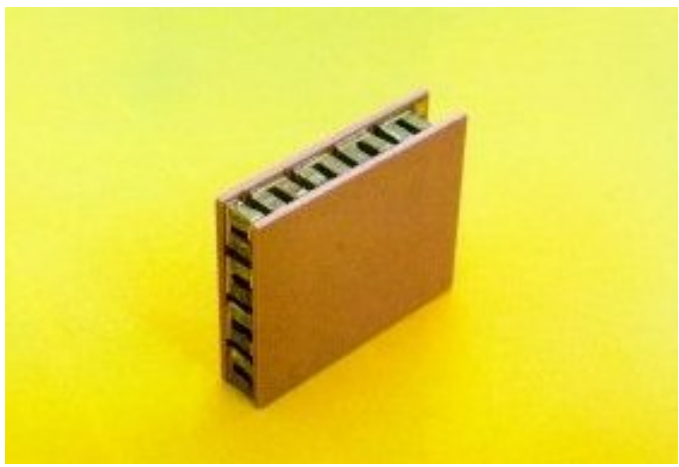
Krasnoyarsk – 26

Conversion production

Model of silicon plant

Semiconductor silicon

High purity tellurium



Thermoelectric module

High purity gallium

Institute of automation and electrometry SB RAS and "Krasmash" factory

Silicon crystal puller and controls panel

20th CODATA conference Beijing
24th October 2006

Institute of automation and electrometry SB RAS and "Krasmash" factory

Test run of the silicon crystal puller

20th CODATA conference Beijing
24th October 2006

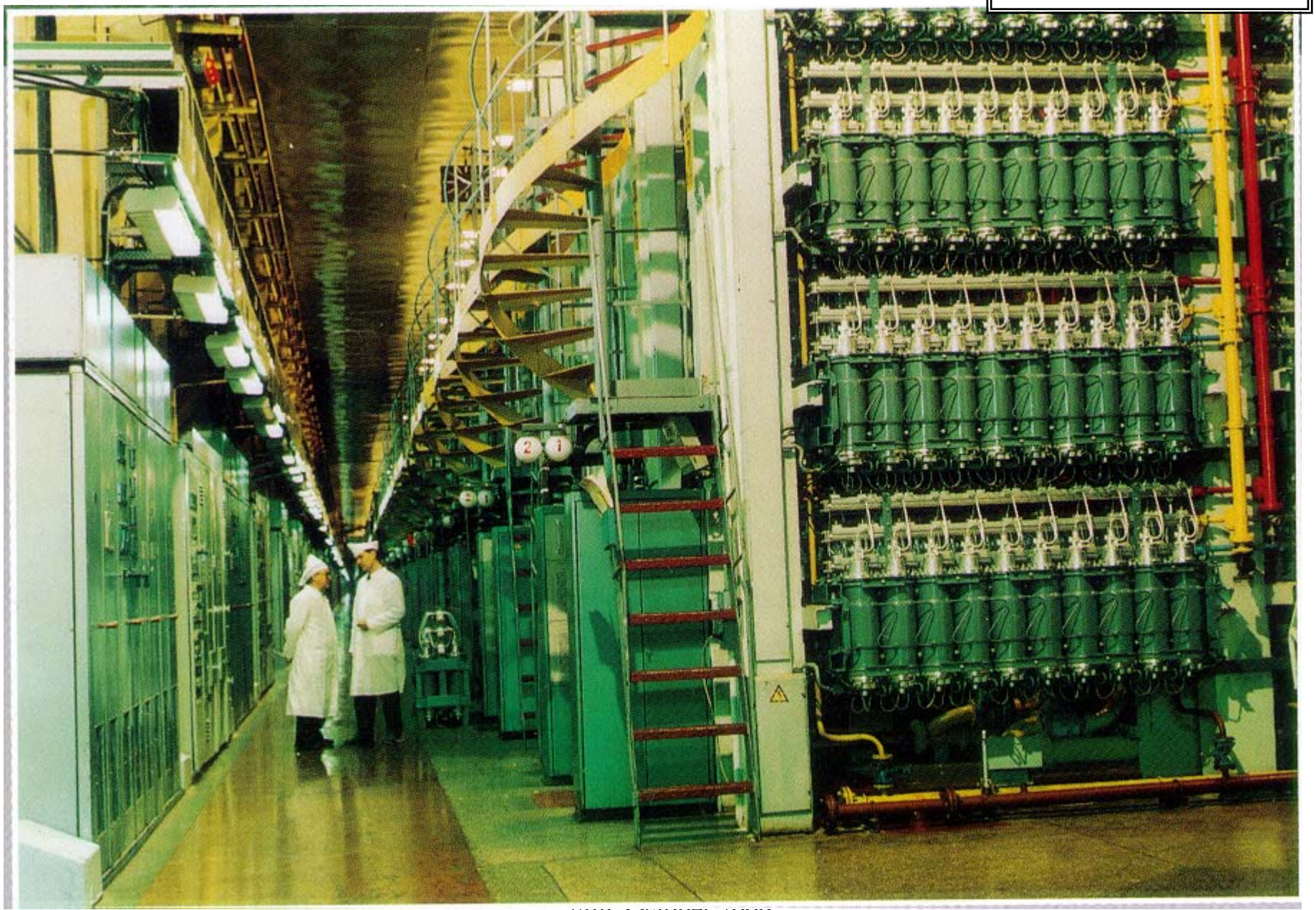
Seversk, Siberian Chemical Combine

Seversk, Siberian Chemical Combine

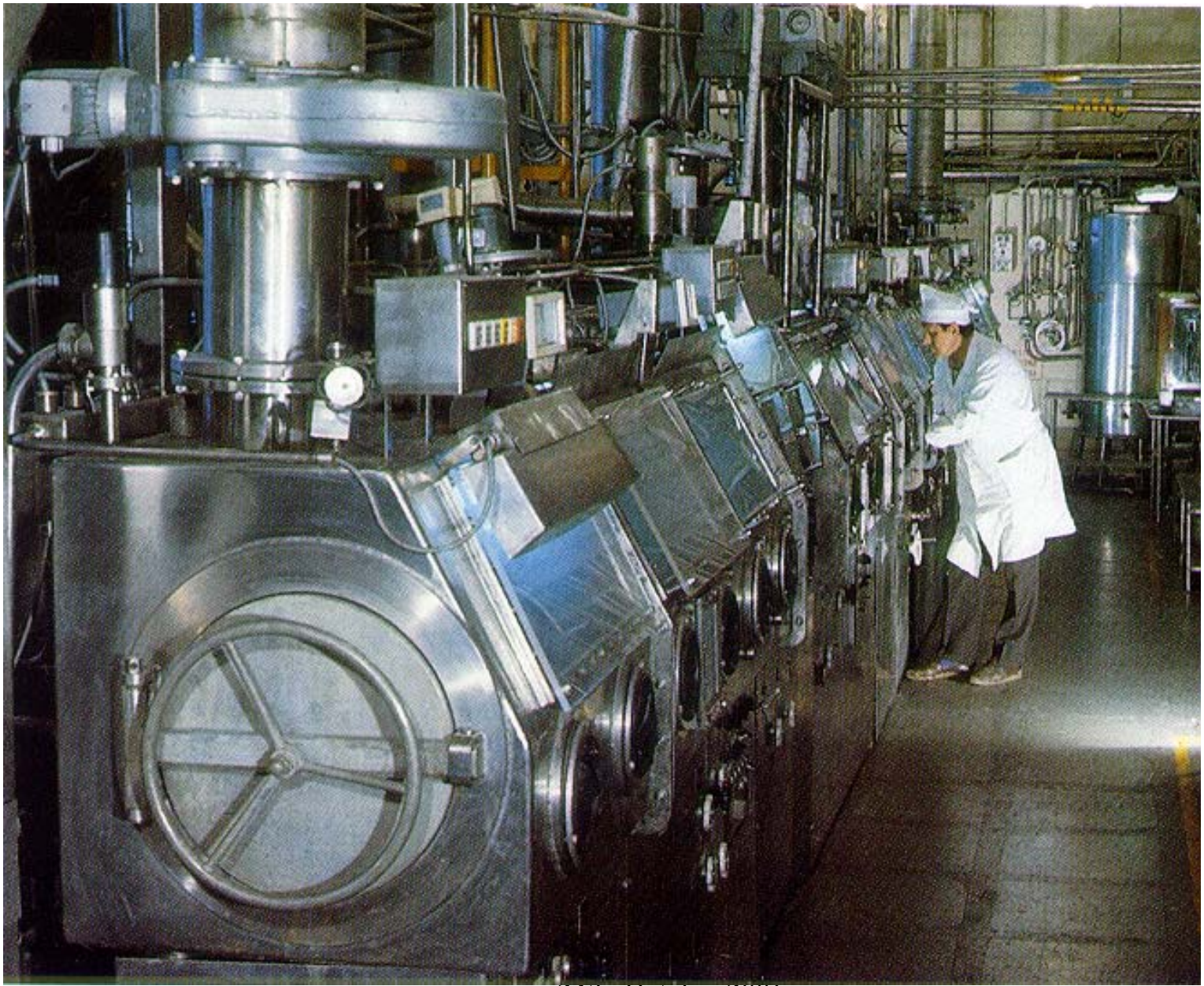
Tomsk – 7

Seversk, Siberian Chemical Combine

Tomsk – 7

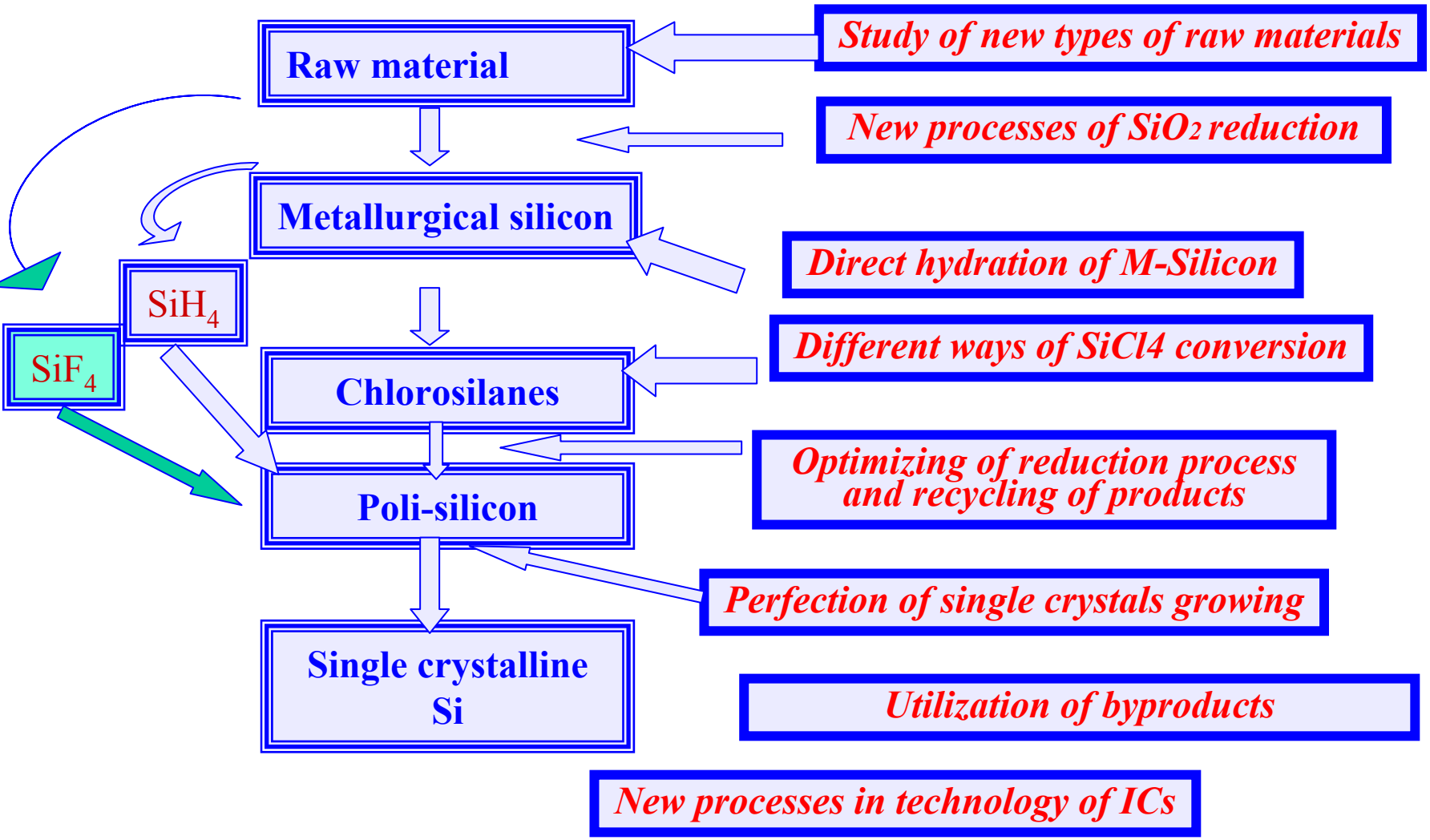


Seversk, Siberian Chemical Combine



Tomsk – 7

Contribution to Silicon processing



Considered schemes of Si production

Нынешняя схема КГХК

$SiO_2 \rightarrow SiHCl_3 \rightarrow Si_{Poly} + SiCl_4 \rightarrow Si_{mono} \rightarrow Si_{пластины} \rightarrow Si_{приборы} \rightarrow Si_{системы}$

Нынешняя схема НЗХК

$SiCl_4 + \mathbf{LiH} \rightarrow SiH_4 \rightarrow Si^*_{Poly} \rightarrow Si^*_{mono} \rightarrow Si^*_{пластины} \rightarrow Si^*_{приборы} \rightarrow Si_{системы}$

Альтернативная схема НЗХК

$SiO_2 + \mathbf{LiH} \rightarrow SiH_4 \rightarrow Si^*_{Poly} \rightarrow Si^*_{mono} \rightarrow Si^*_{пластины} \rightarrow Si^*_{приборы} \rightarrow Si_{системы}$

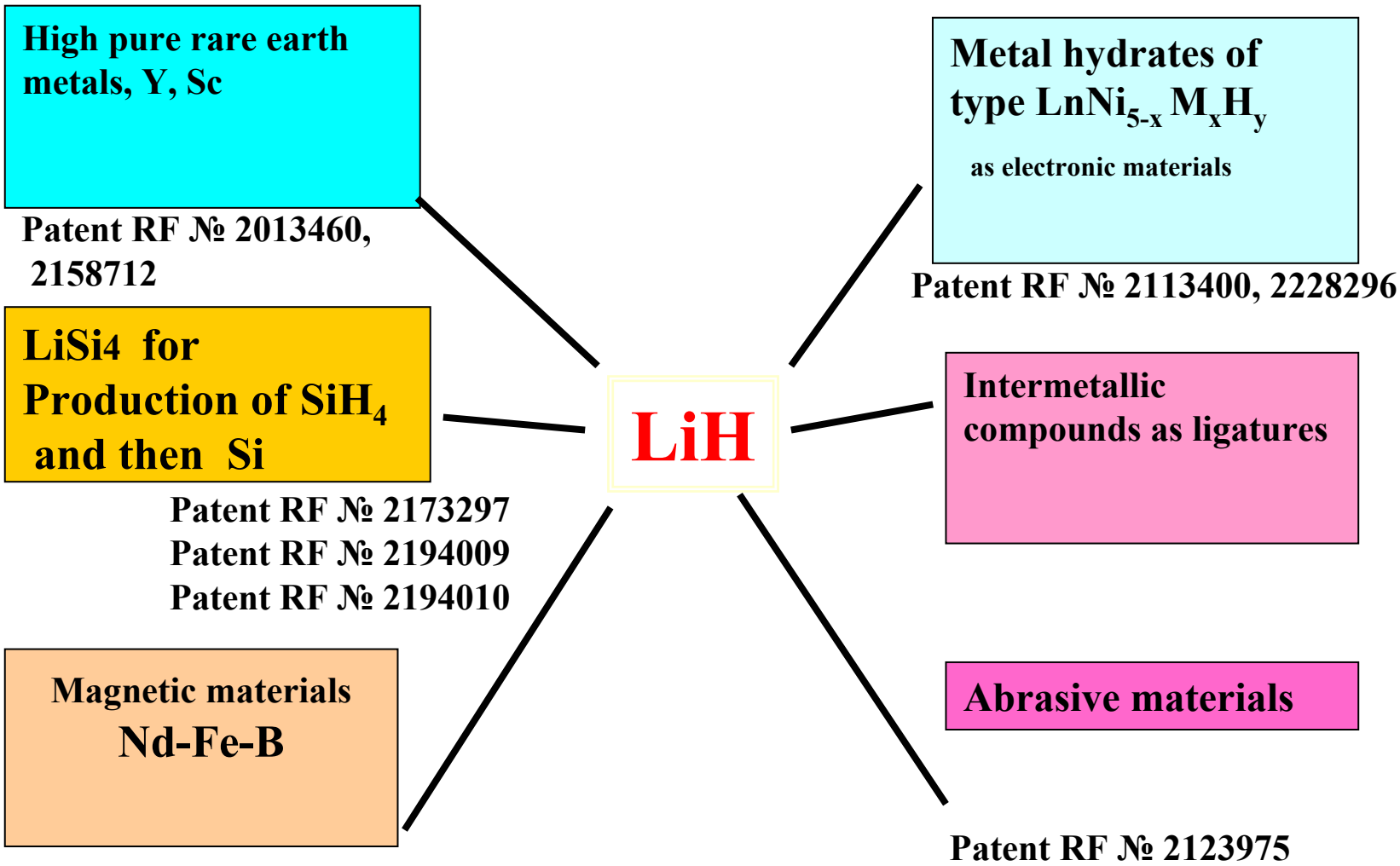
ОНЗХК

ИБИРСКИЙ ЗАВОД ХИМКОНЦЕНТРАТОВ

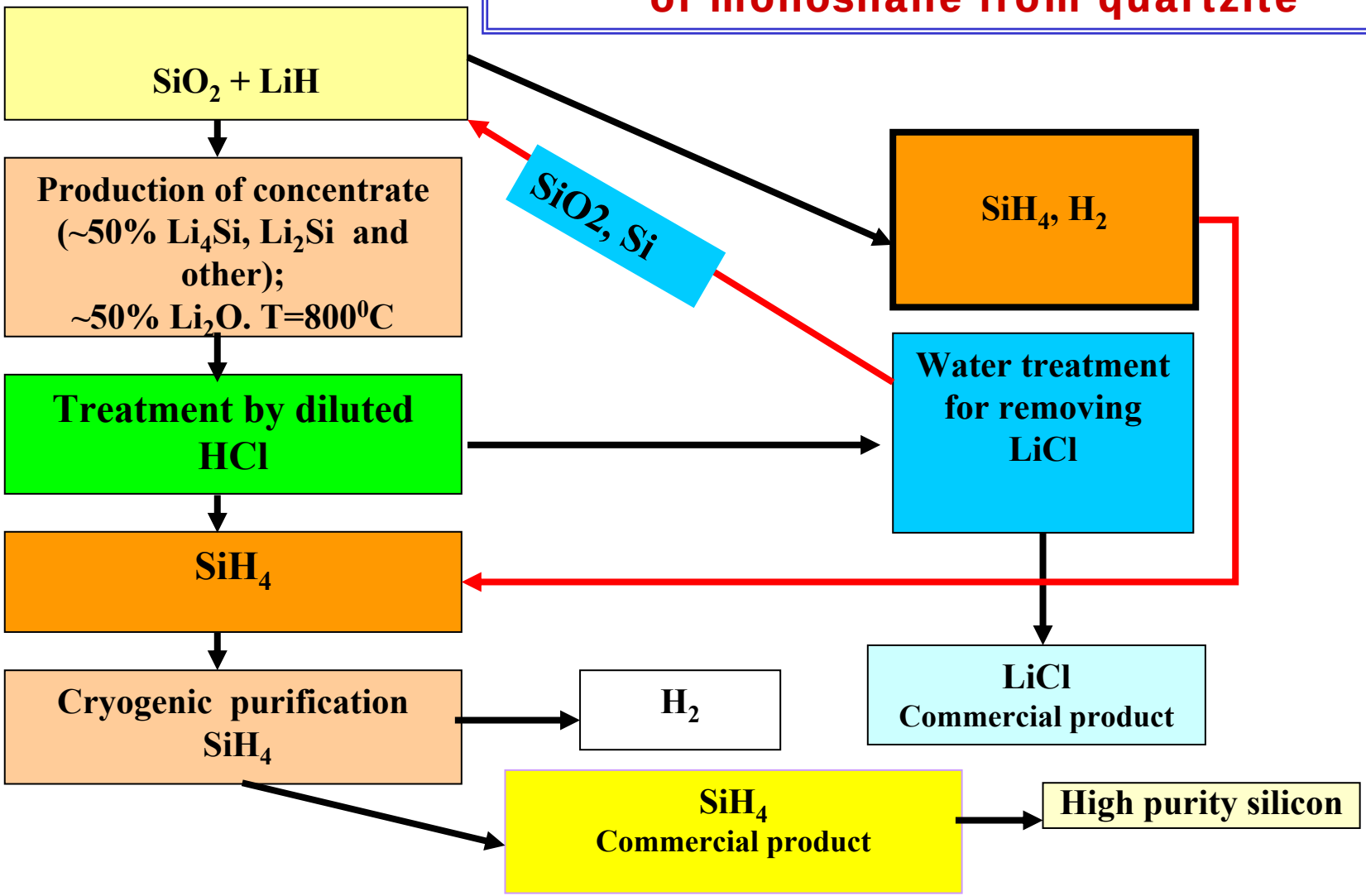
Novosibirsk chemical concentrates factory

Joint-stock company the Novosibirsk chemical concentrates factory - one of the largest enterprises of Russia, producing **nuclear fuel for the atomic power stations** and research reactors, **lithium and its compounds** . The basic directions of activity of the enterprise are: Uranium manufacture; ВВЭР-1000; ВВЭР-440; Li manufacture; Manufacture of products of physical chemistry.

Use of LiH in materials synthesis



Scheme of LiH technology for production of monosilane from quartzite



Почему мультикремний?

- Значительно более низкая стоимость получения слитка мультикремния по сравнению с монокристаллом

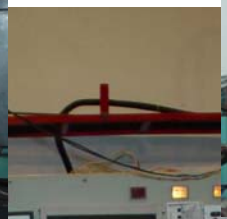
- Небольшая разница в эффективности солнечных элементов на основе мультикремия и монокристалла-

14,5% МКК и 16% МК (комерч)

22,7% МКК и 24% МК (лабор)

- Гораздо меньшие отходы при изготовлении пластин

Физико-химические основы технологии получения мультикремния



Эксперимент

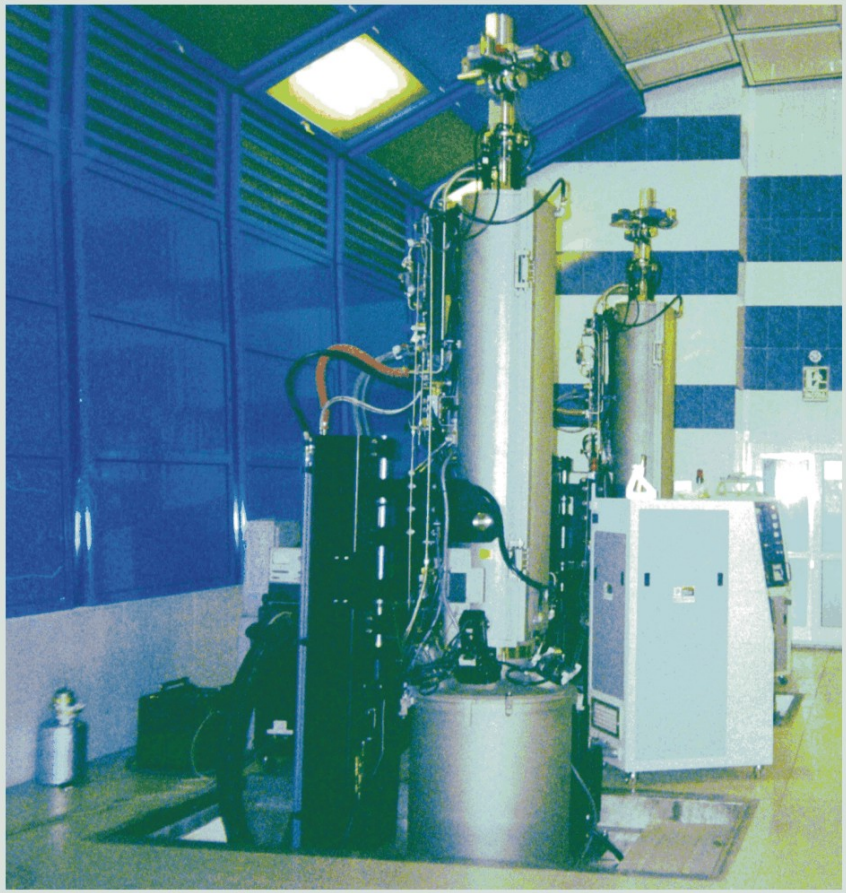
- Февраль 1999: *получение высокочистого кремния на одной из 25 MVA печей ЗАО «Кремний»*

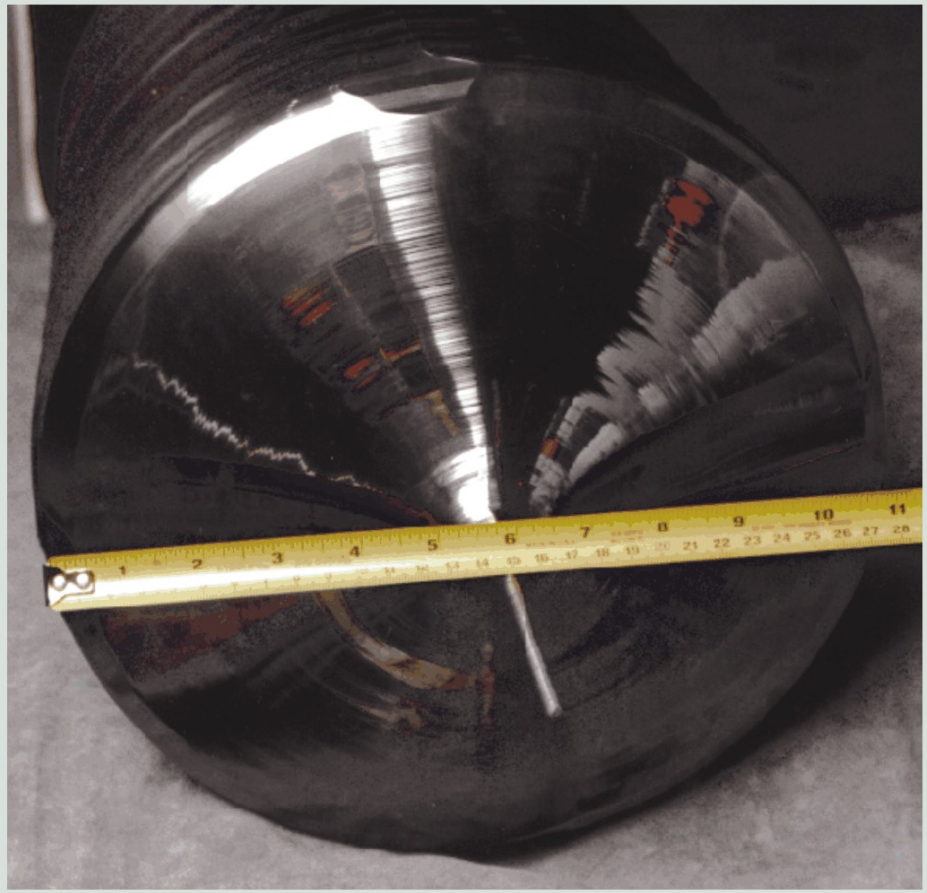
Silicon of KMCC

Silicon of Institute of Physics SB RAS

СИБИРСКОЕ ОТДЕЛЕНИЕ РАН

Министерство по атомной энергии РФ

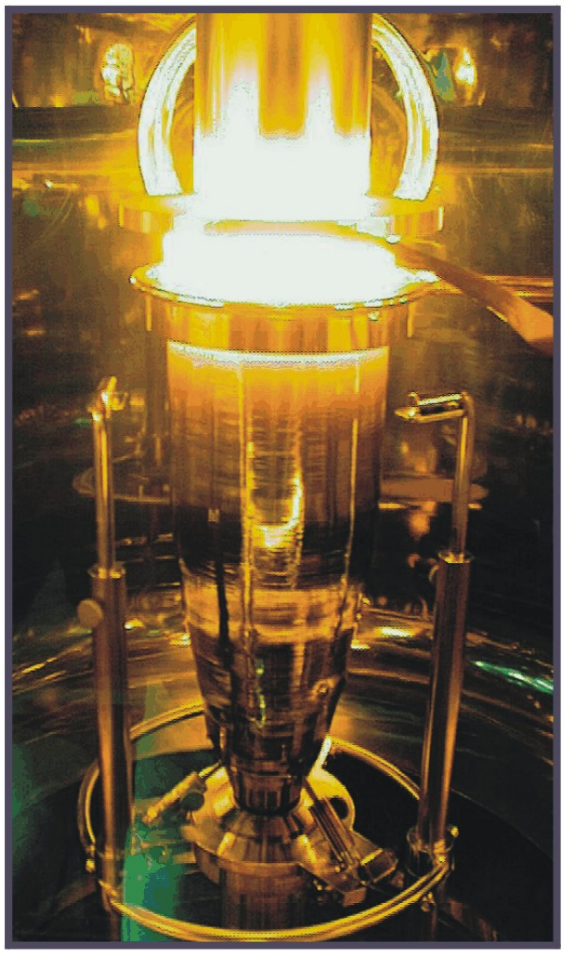




Марки кремния, выращиваемые методом Чохральского на Красноярском горно-химическом комбинате
(общий объем продаж более 300 кг/мес.)

Тип материала	КДБ-0,01; КДБ-12; КЭФ - 4,5; "Солнечный кремний"
Удельное электросопротивление, Ом*см	0,01 - 0,02; 12; 4,5; 5 - 20
Время жизни н.н.з., мкс	48, 40, > 20
Диаметр, мм	150 - 200, 150, 150, 125 -150

РОСТ МОНОКРИСТАЛЛОВ КРЕМНИЯ МЕТОДОМ БЕСТИГЕЛЬНОЙ ЗОННОЙ ПЛАВКИ



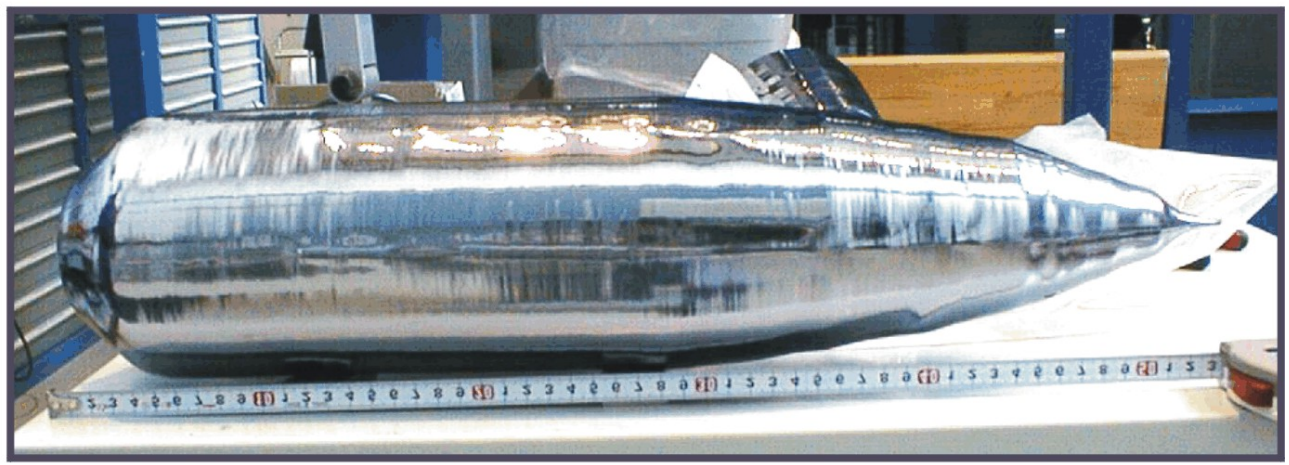
Индукционный переплав поликремния и рост кристалла диаметром 100 мм

Марки кремния, выращиваемые методом бестигельной зонной плавки в ИФП СО РАН (общий объем продаж - 250 кг/год)

Диаметр слитков, мм	40 - 125
УЭС после выращивания, Ом*см	1000 - 100 000
УЭС после нейтронного легирования, Ом*см	25 - 320
Время жизни н.н.з., мкс	50 - 4 000

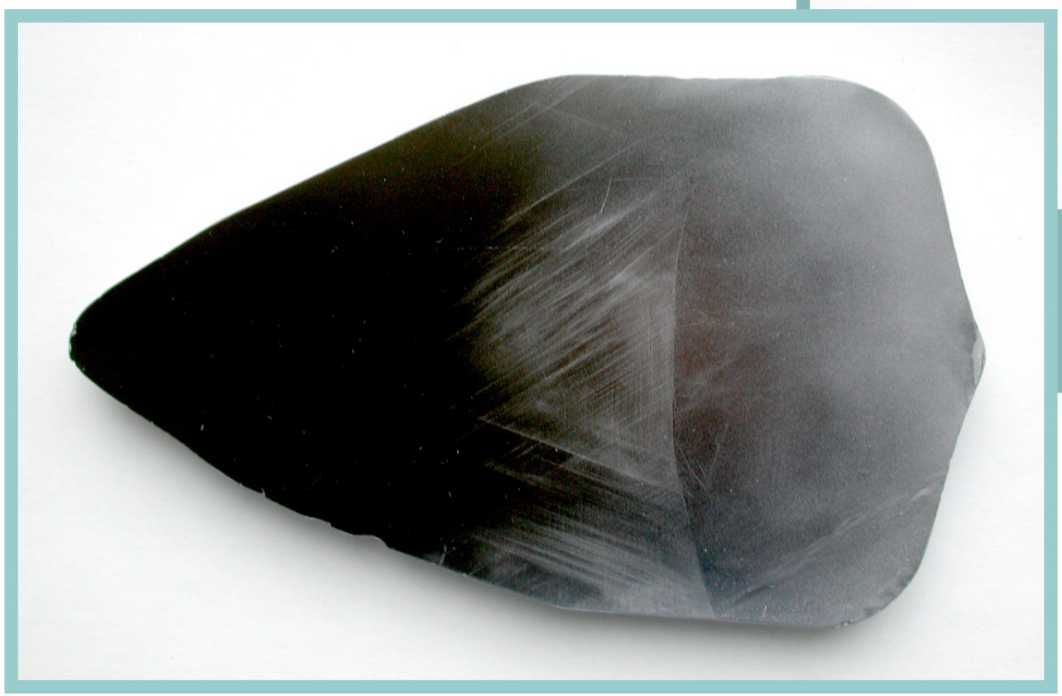
Основные потребители

ОАО “Искра” (Ульяновск); ОАО “Электровыпрямитель” (г. Саранск);
ЗАО “Протон-электротекс” (г. Орел); ОАО “Ангстрем” (г. Зеленоград);
ПО “Интеграл” (Белоруссия); ОАО “Силовая электроника Сибири” (Новосибирск).



Кристалл диаметром 125 мм, выращенный на установке FZ-20

ВЫРАЩИВАНИЕ МОНОКРИСТАЛЛИЧЕСКОГО КРЕМНИЯ МЕТОДОМ БЕСТИГЕЛЬНОЙ ЗОННОЙ ПЛАВКИ

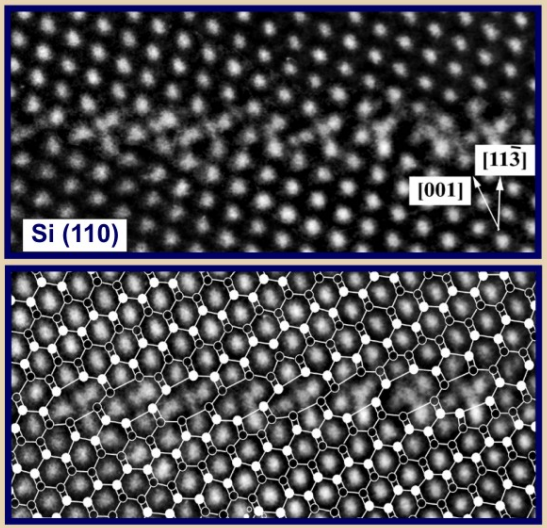


Распределение дефектов
по поперечному срезу слитка

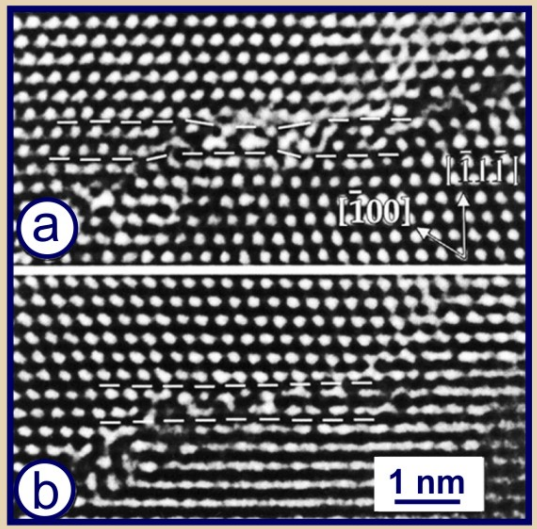
ИНСТИТУТ ФИЗИКИ ПОЛУПРОВОДНИКОВ

Реакции точечных дефектов в высокосовершенных кристаллах БЗП-кремния

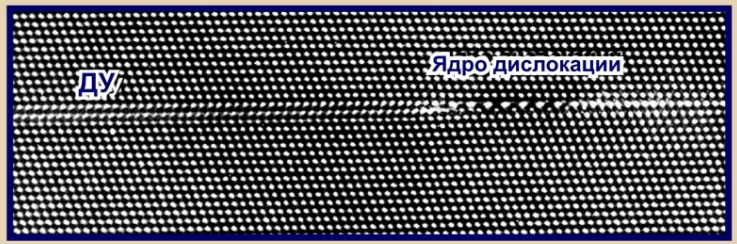
Метастабильные конфигурации междоузельных атомов в ядре дислокации Франка вкристалле кремния

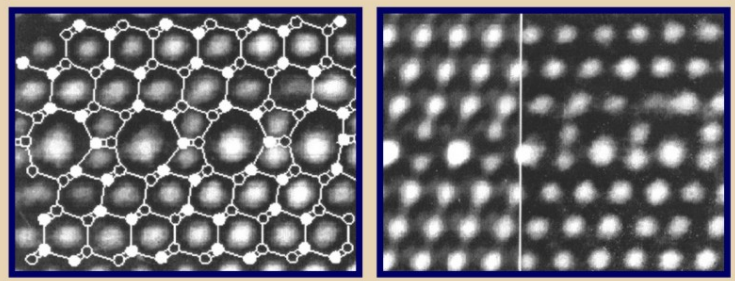


Скопление вакансий по плоскости (113) в кристалле БЗП-кремния



Последовательные стадии формирования вакансионно-междоузельного кластера в кремнии



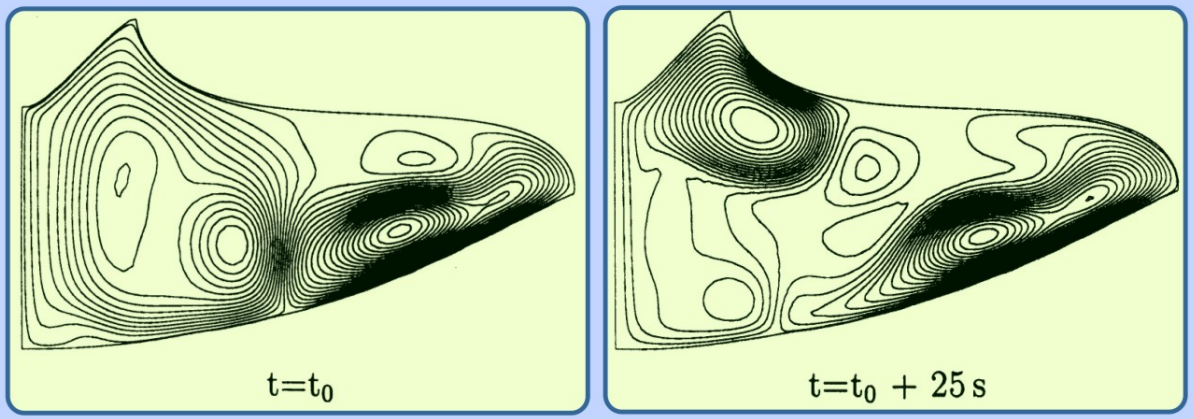


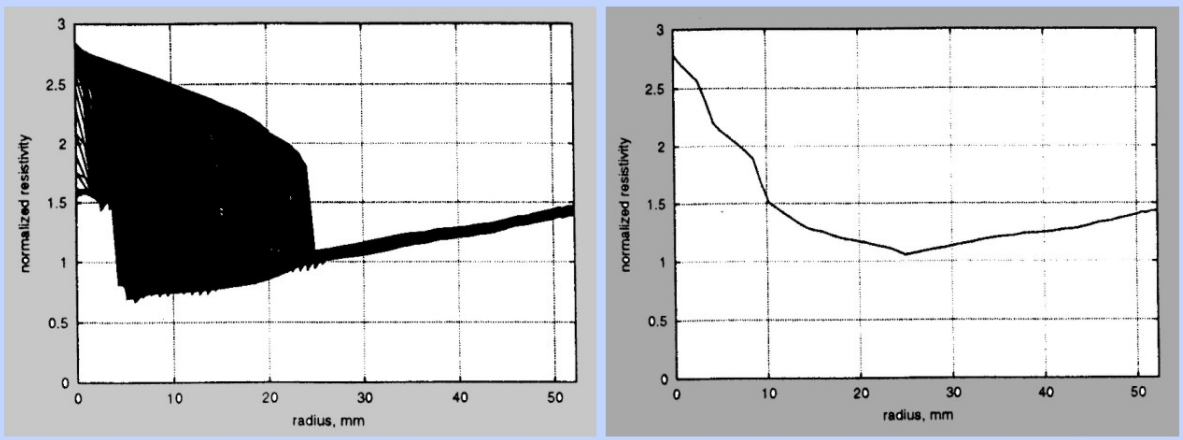
На основе in situ экспериментов по облучению полупроводниковых кристаллов электронами в ВРЭМ исследованы реакции взаимодействия точечных дефектов между собой, с атомами примесей, поверхностью и дислокациями. Установлено, что особенности этих реакций определяются метастабильными конфигурациями точечных дефектов в алмазоподобной кристаллической решетке

Л.И. Федина, А.Л. Асеев
В кн: Нанотехнологии в полупроводниковой электронике, изд. СО РАН, Новосибирск, 2004, § 3.2, с. 279-201

ИНСТИТУТ ФИЗИКИ ПОЛУПРОВОДНИКОВ СО РАН
INSTITUTE FOR ELECTROHEAT, UNIVERSITY OF HANOVER

Расчетные данные для потоков в расплаве и электросопротивление слитков вдоль фронта кристализации при бестигельной зонной плавке кремния

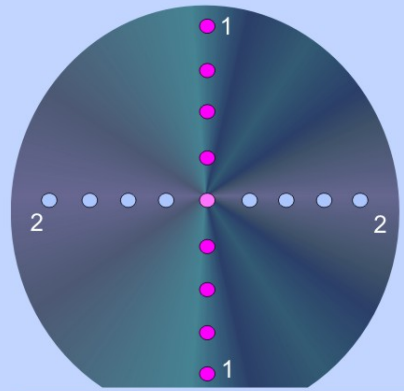


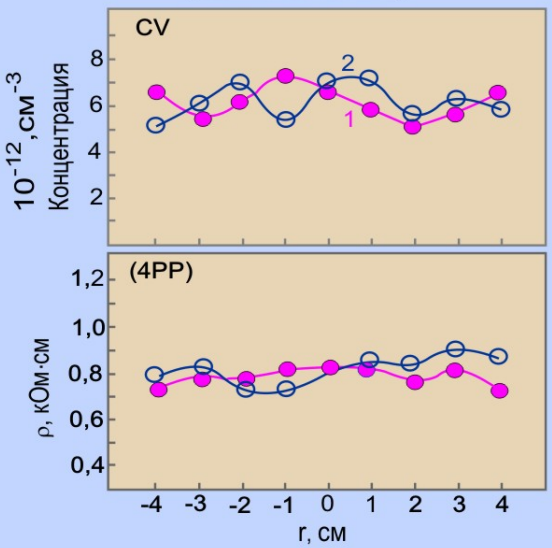


Осцилляции электросопротивления

Среднее значение электросопротивления

Радиальное распределение концентрации легирующей примеси и электросопротивления в пластинах БЗП-кремния

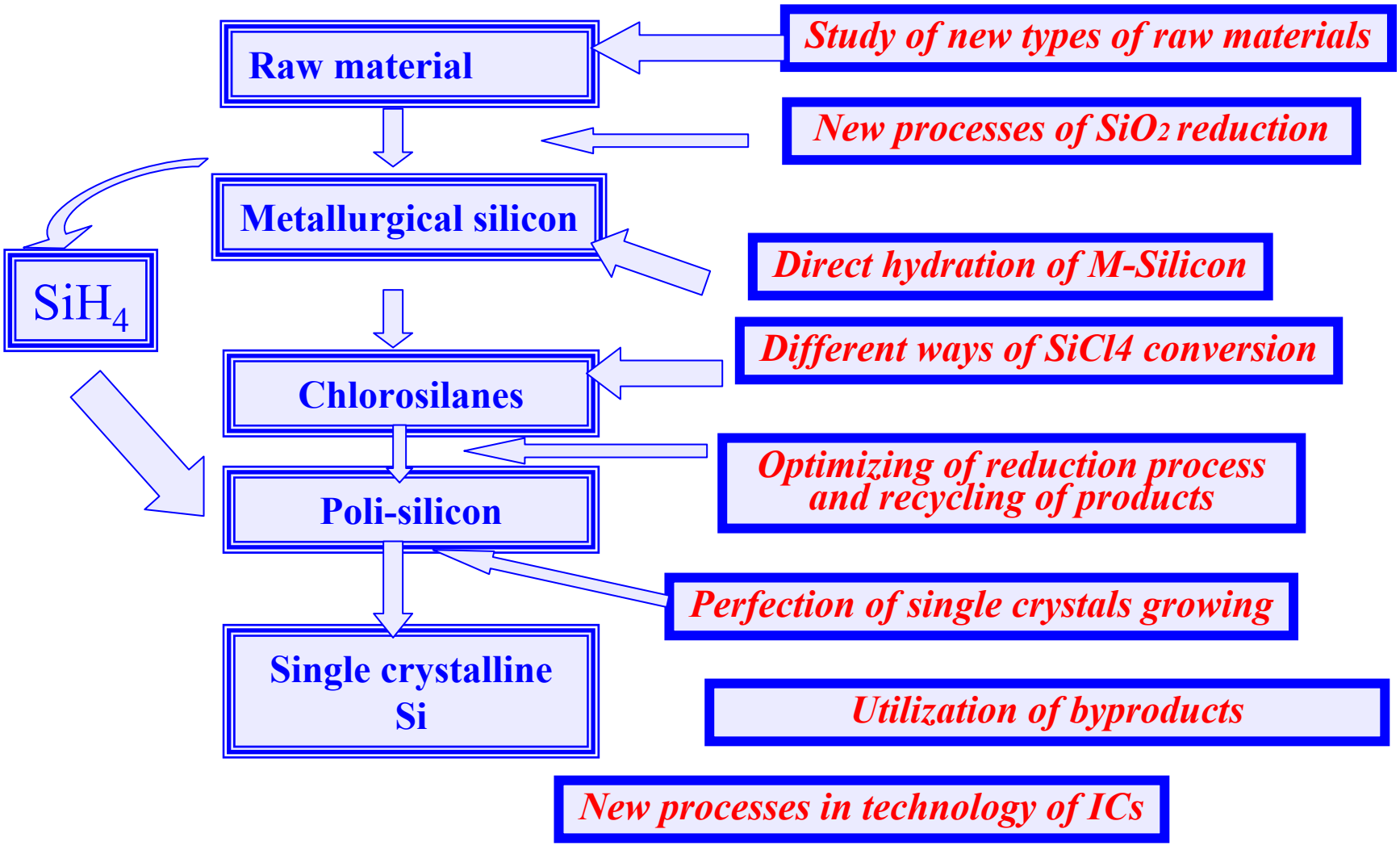




Some joint material science and technology projects with FAAE enterprises

20th CODATA conference Beijing
24th October 2006

Contribution to Silicon processing

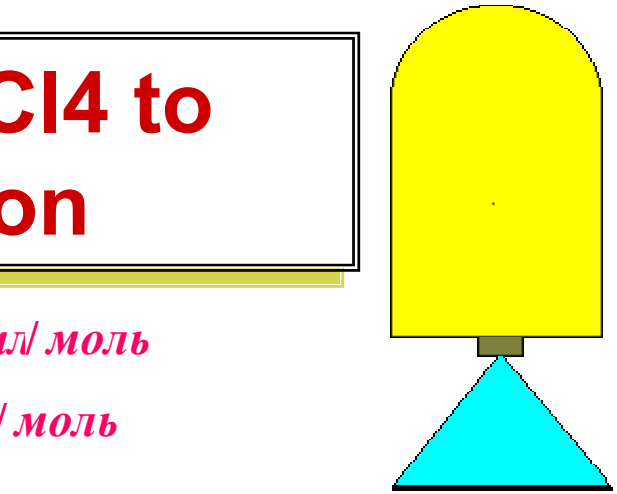


E-beam initiated SiCl4 to SiHCl3 conversion

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl, \ldots \Delta H^\circ = 16{,}5 Ккал/моль$$

$$SiCl_4 \rightarrow SiCl_3 + Cl, \ldots\ldots\ldots\ldots \Delta H^\circ = 111 Ккал/моль$$

$$H_2 \rightarrow H + H, \ldots\ldots\ldots\ldots\ldots\ldots \Delta H^\circ = 105 Ккал/моль$$



$SiCl_4 + H_2$

$\downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow$

$SiCl_4^+ + SiCl_3^+ + H^+ + H$

$Cl^- + ne^- + \hbar\omega$

$\downarrow \oplus \downarrow \cdot \downarrow \oplus \downarrow \cdot \downarrow \oplus \downarrow \cdot \downarrow$

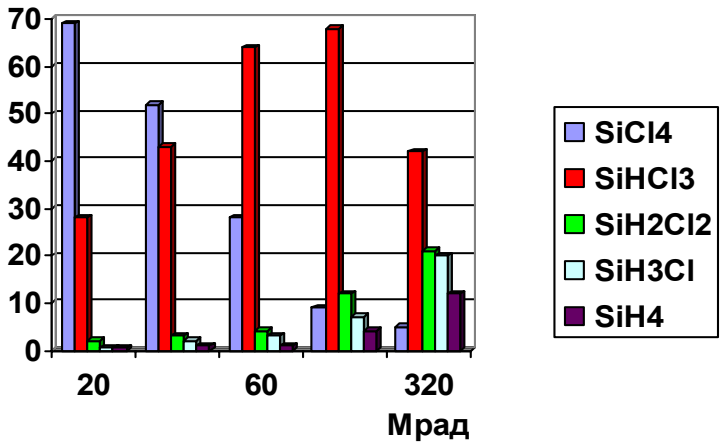
$\downarrow * \downarrow \cdot \downarrow * \downarrow \cdot \downarrow * \downarrow \cdot \downarrow * \downarrow$

$SiCl_4 + SiHCl_3 + SiCl_3^+ +$

$SiHCl_2^+ + SiCl_2^+ + SiH_2Cl_2$

$HCl + H^+ + H + me^- + \hbar\omega$

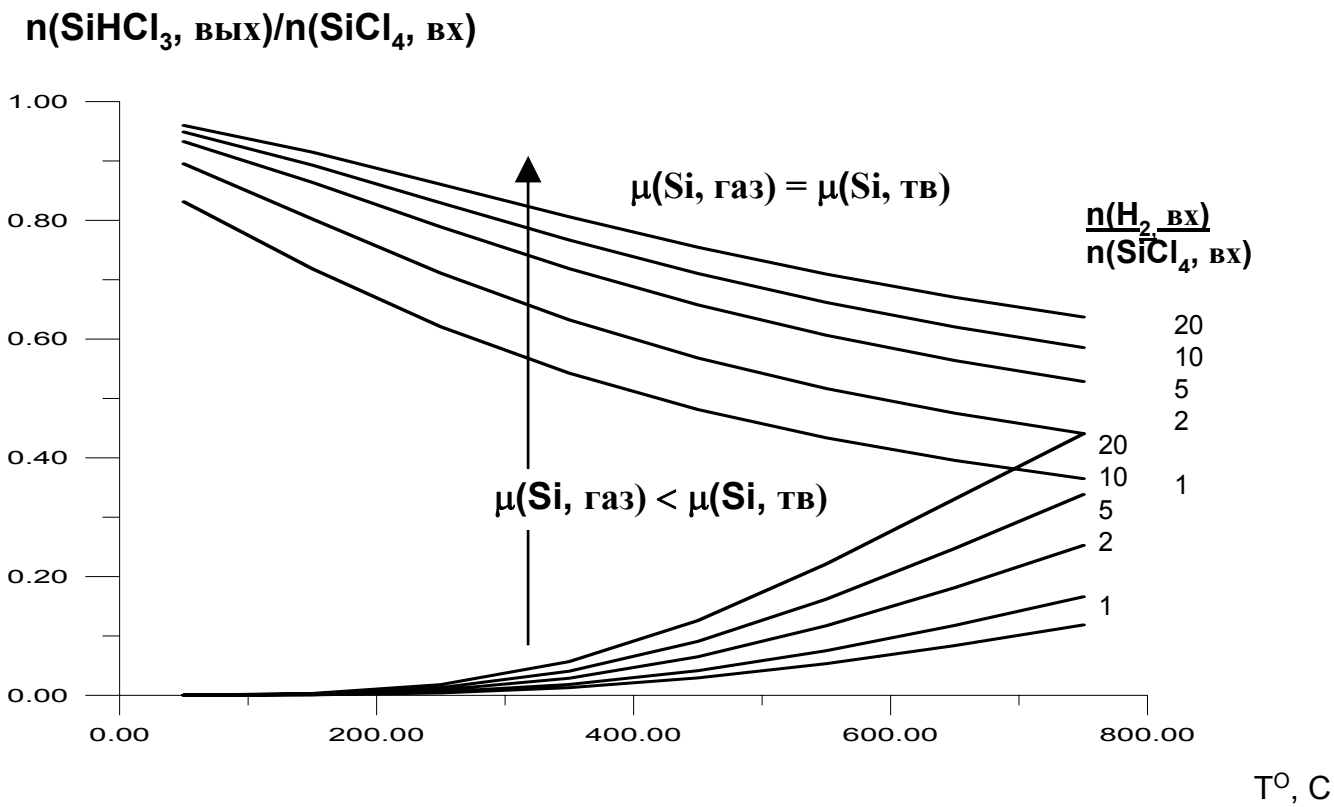
$\downarrow \bullet \downarrow \circ \downarrow \bullet \downarrow \circ \downarrow \bullet \downarrow \circ \downarrow \bullet \downarrow$



$SiHCl_3 + HCl + H_2$

$SiCl_4 + SiH_2Cl_2 + SiH_3Cl + SiH_4$

Optimization of Si technology
E-beam conversion of tetrachloride

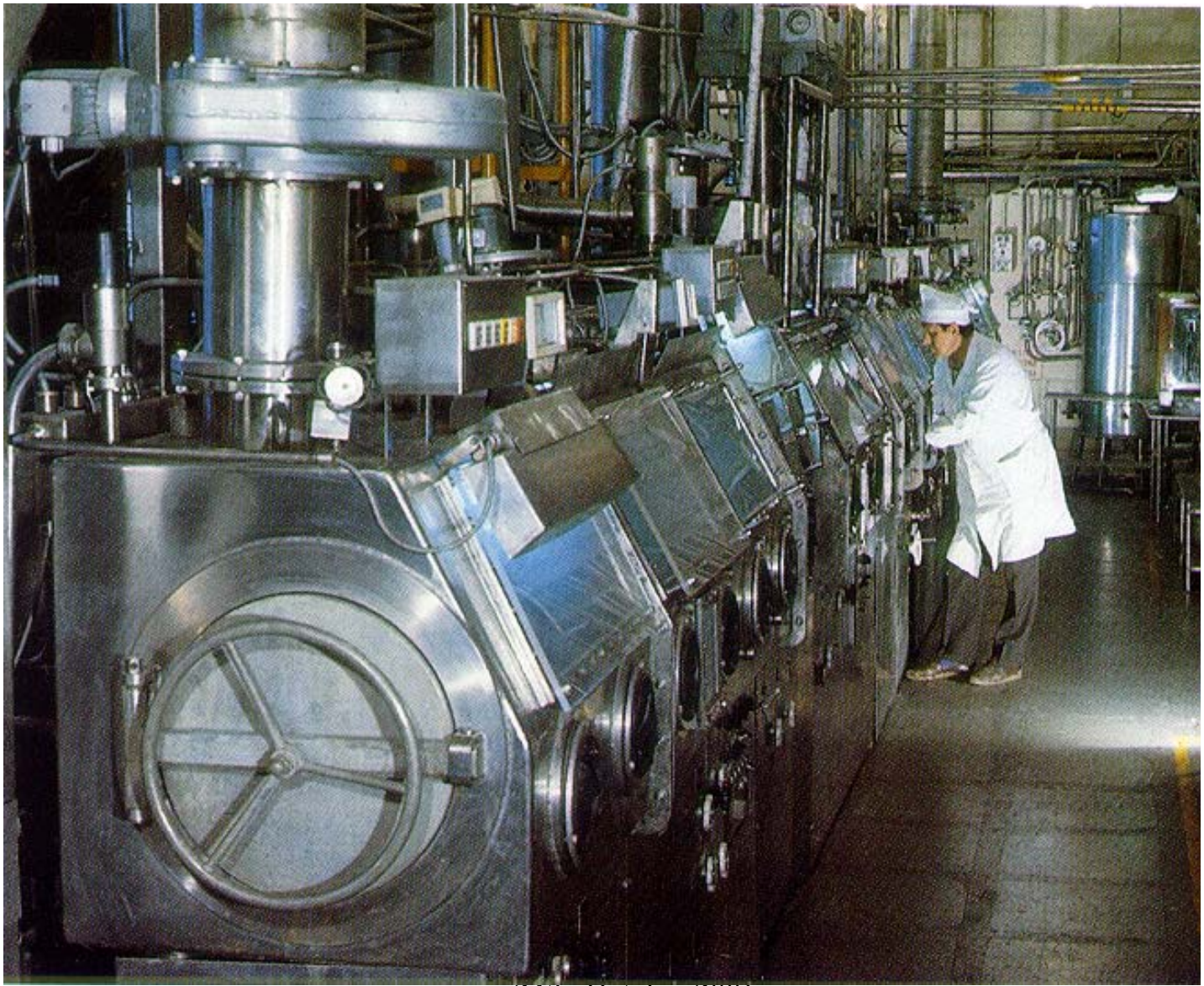


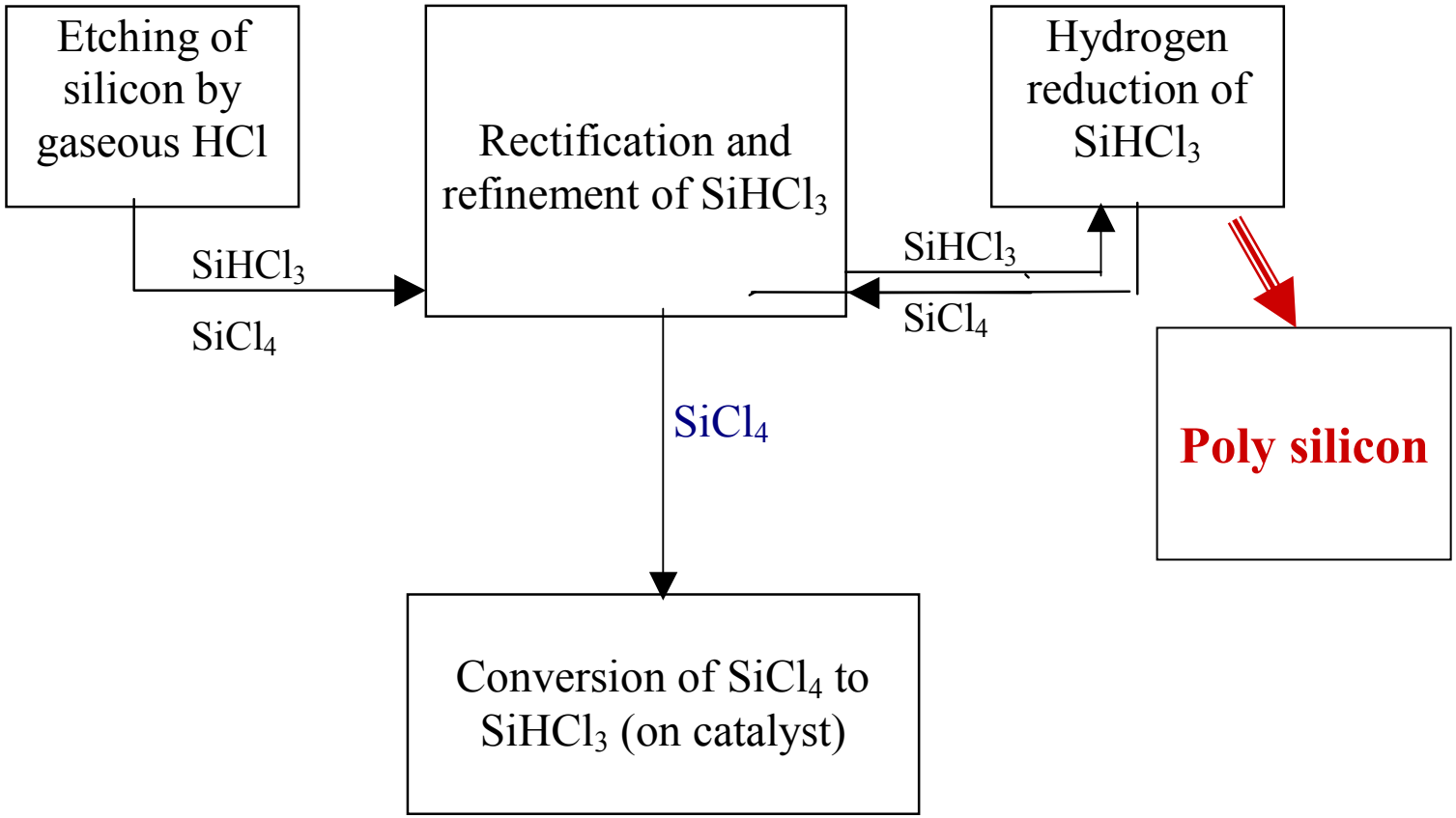
Рост выхода $SiHCl_3$ при принудительном увеличении μ (Si,газ)

LI-Si technology

Схема гидрид-литиевой технологии производства высокочистого моносилана из тетрахлорида кремния (ИНХ СО РАН, НЗХК)

Fluorine processing





The yield of process (~35%) is near theoretical.

The alternative ways for catalytic conversion:

Conversion of $SiCl_4$ in reactor of etching

The low-temperature energy-stimulated processes of $SiCl_4$ conversion