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GeSiR Final Project Meeting

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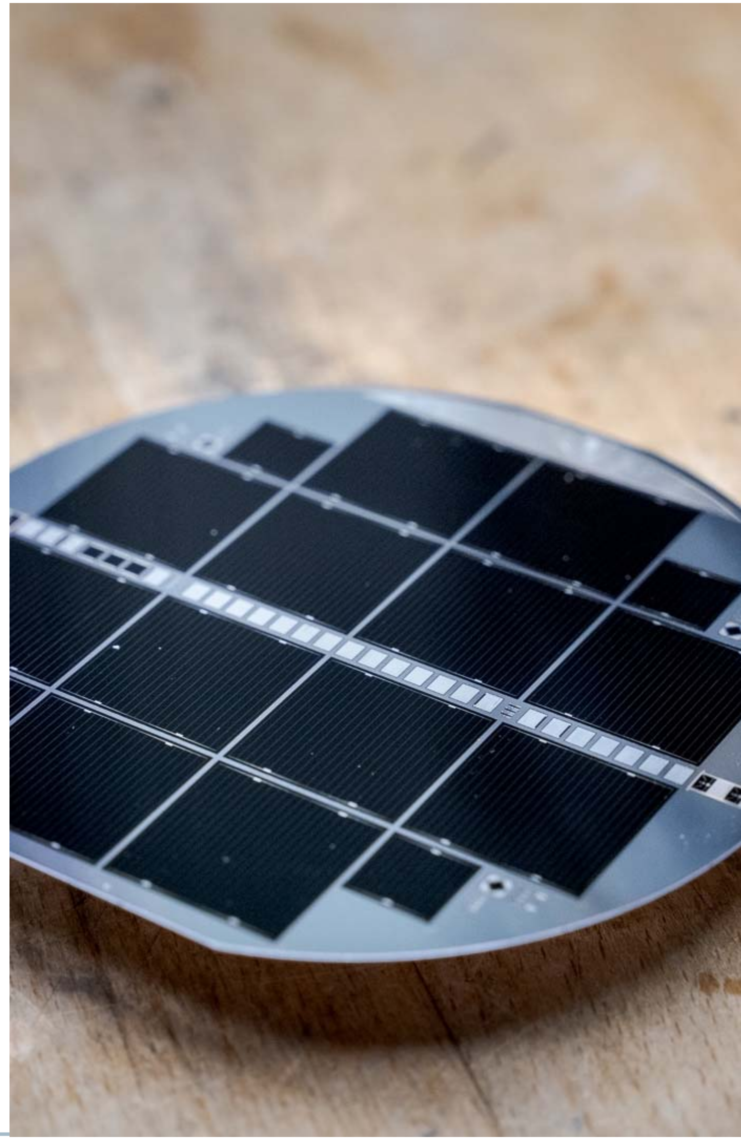
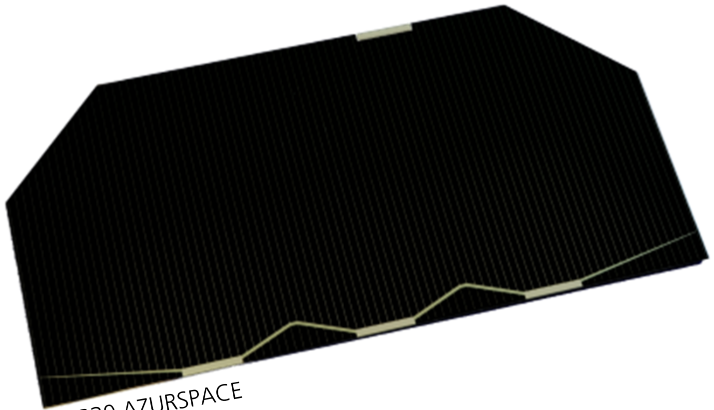
Content

Low Ge Alternative Space Triple Junction Solar Cells on SiGe Engineered Substrates and Ge Recovery from Grinding Slurry of Wafer Thinning



Motivation

- Germanium is a critical raw material, yet it is the basis of today‘s European space solar cells
- We assume about 2 tons of Ge is sent to space in solar cells every year
- Ge wafers have high environmental impact
  - Ge sourcing from coal ashes or mining
  - Ge puryfing, crystal pulling, wafering….



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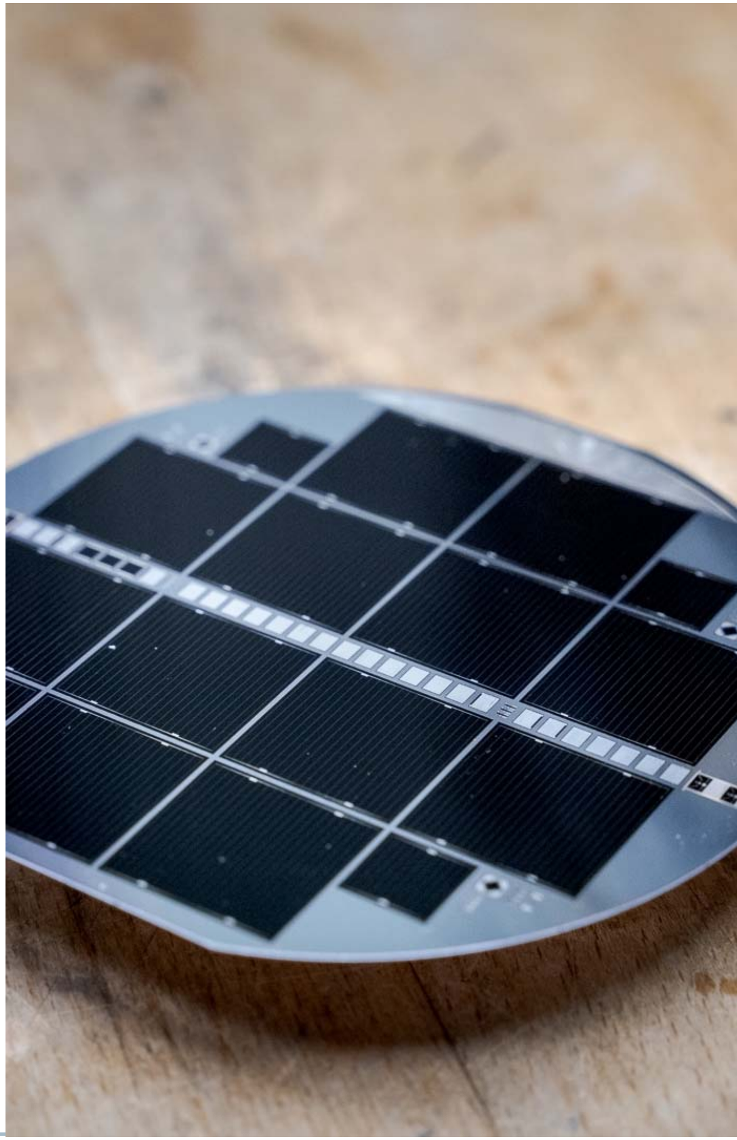
Content



Ge Recovery from Grinding Slurry

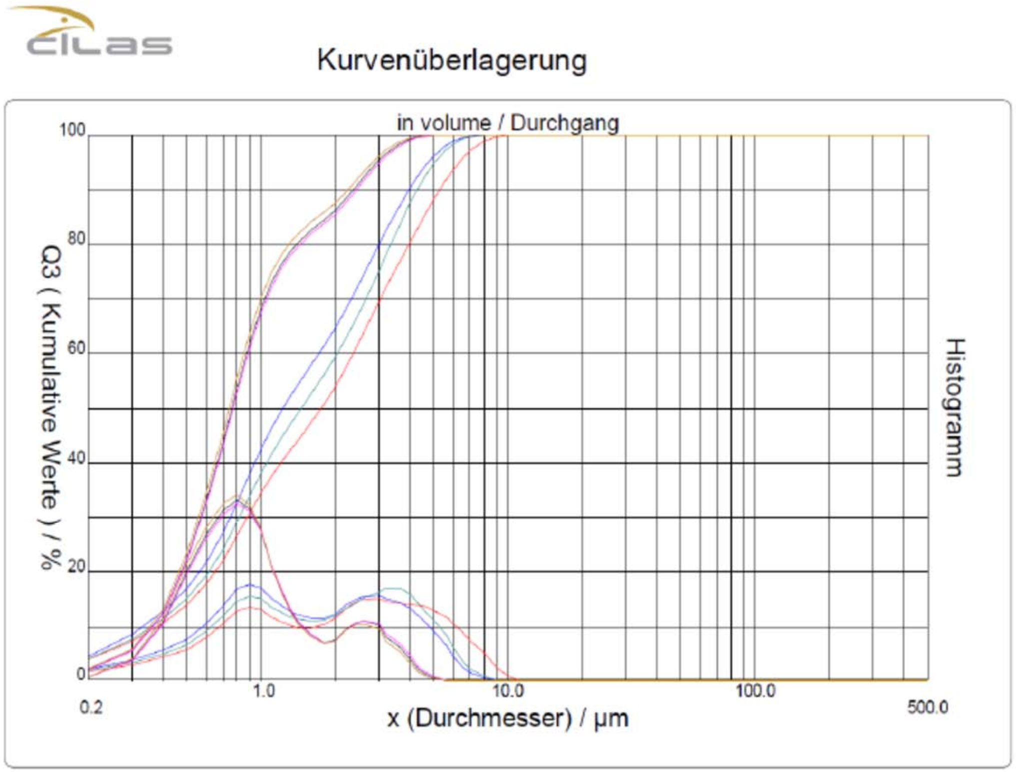
- Ge wafer serve as growth substrate and bottom junction. A certain thickness is needed for high yield during epitaxy and photolithography processes

- Ge is relatively heavy - thus for weight (and thus cost) reasons, substrates are thinned by grinding at end of processing

→ How to recyle Ge from the grinding slurry (water with little Ge concentration)

Ge Recovery from Grinding Slurry

Analysis of Grinding Waste Water



- Particle size distribution is in the lower **micrometer / sub-micrometer range.**
- Germanium is present as **solid particles** (micrometer, sub-micrometer range) **together with dissolved GeO_2** in aqueous solution
- Germanium concentration is in the range of **50 - 100 g/m³ (50 to 100 ppm).**

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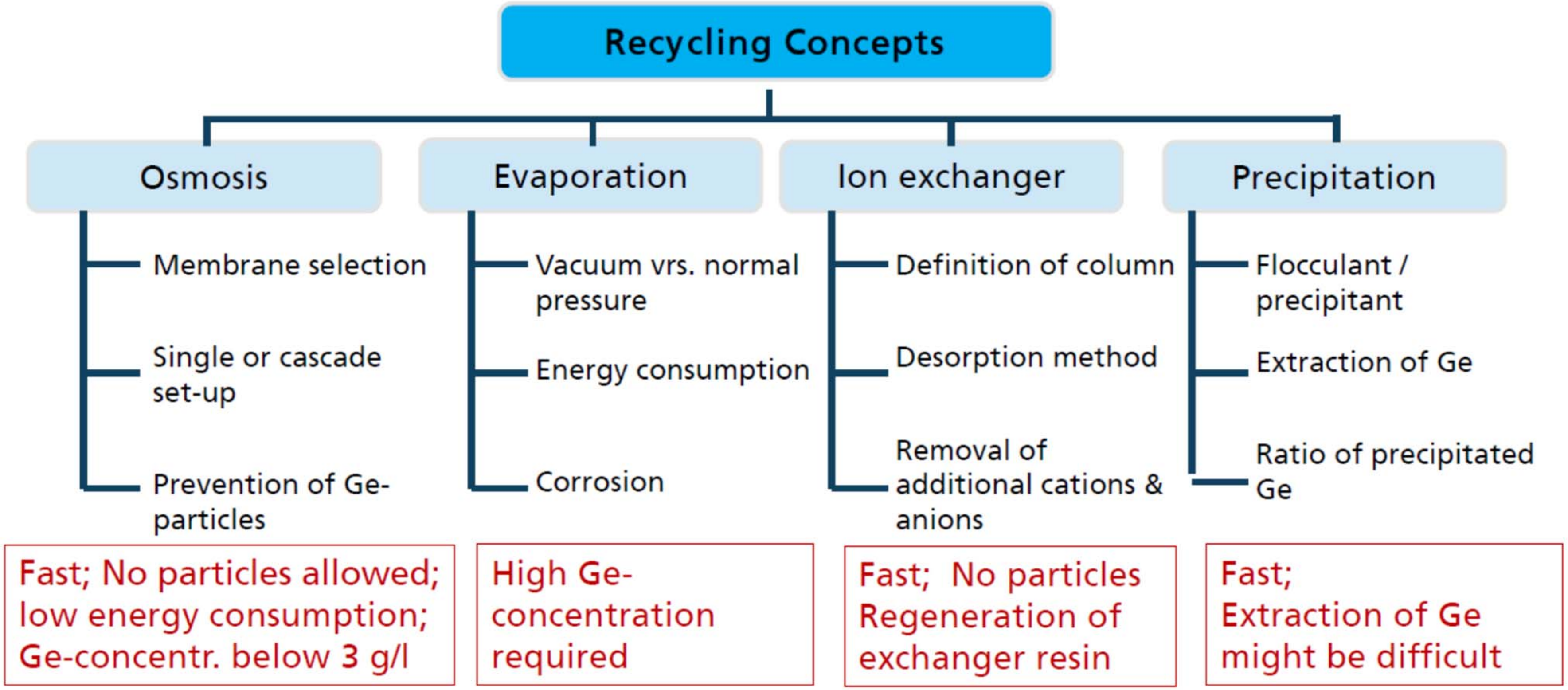
Ge Recovery from Grinding Slurry



Ge Recovery from Grinding Slurry

Analysis of Grinding Waste Water

Table II: Germanium etch rate for aqueous oxidative chemistries.

	Etch rate (nm/min)
H_2O with O_2 bubbling	0.005
H_2O with O_3 bubbling	4
H_2O/H_2O_2 (9/1)	40

A Study of the Influence of Typical Wet Chemical Treatments on the germanium Wafer Surface

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- Maximum solubility of germanium in water:
  - 4 g/l @ RT
  - Around 10 g/l @ T_b
- Dissolution in water:
  - Lack of oxygen: slow
  - Oxidizing agent: fast (up to 1 µm in diameter within 10 minutes)

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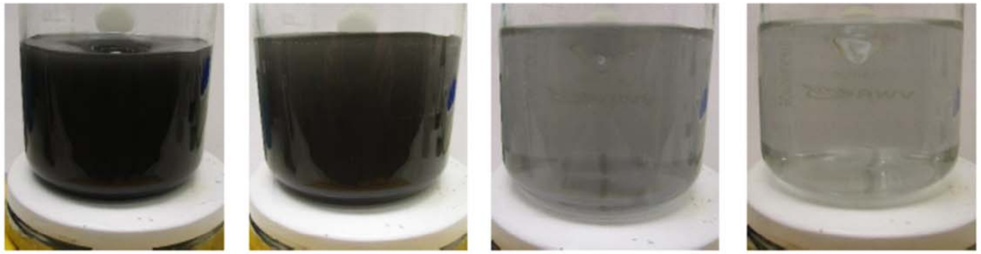
Ge Recovery from Grinding Slurry

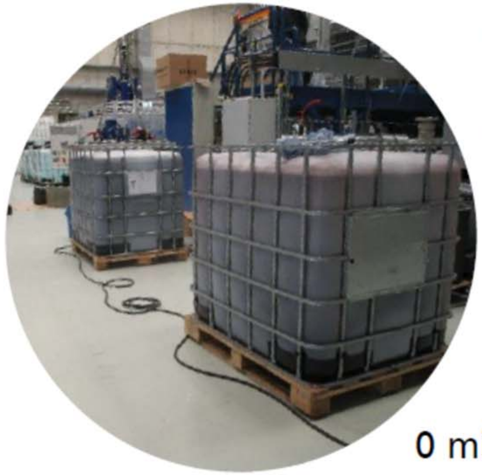
With stirrer

0,5l Ge-grinding water (P1200, 0,13 g/l) 20 drops of H_2O_2 (50%),

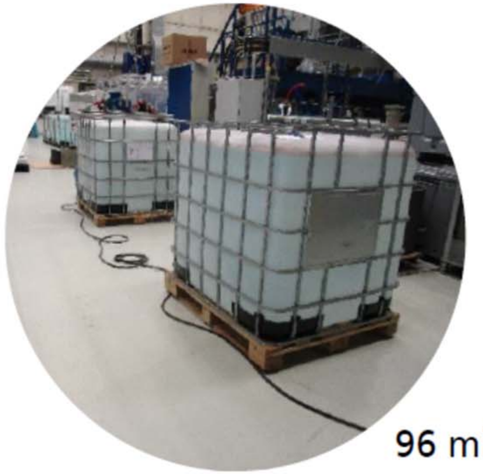


0 min 5 min 10 min 15 min

Without stirrer



0 min



96 min

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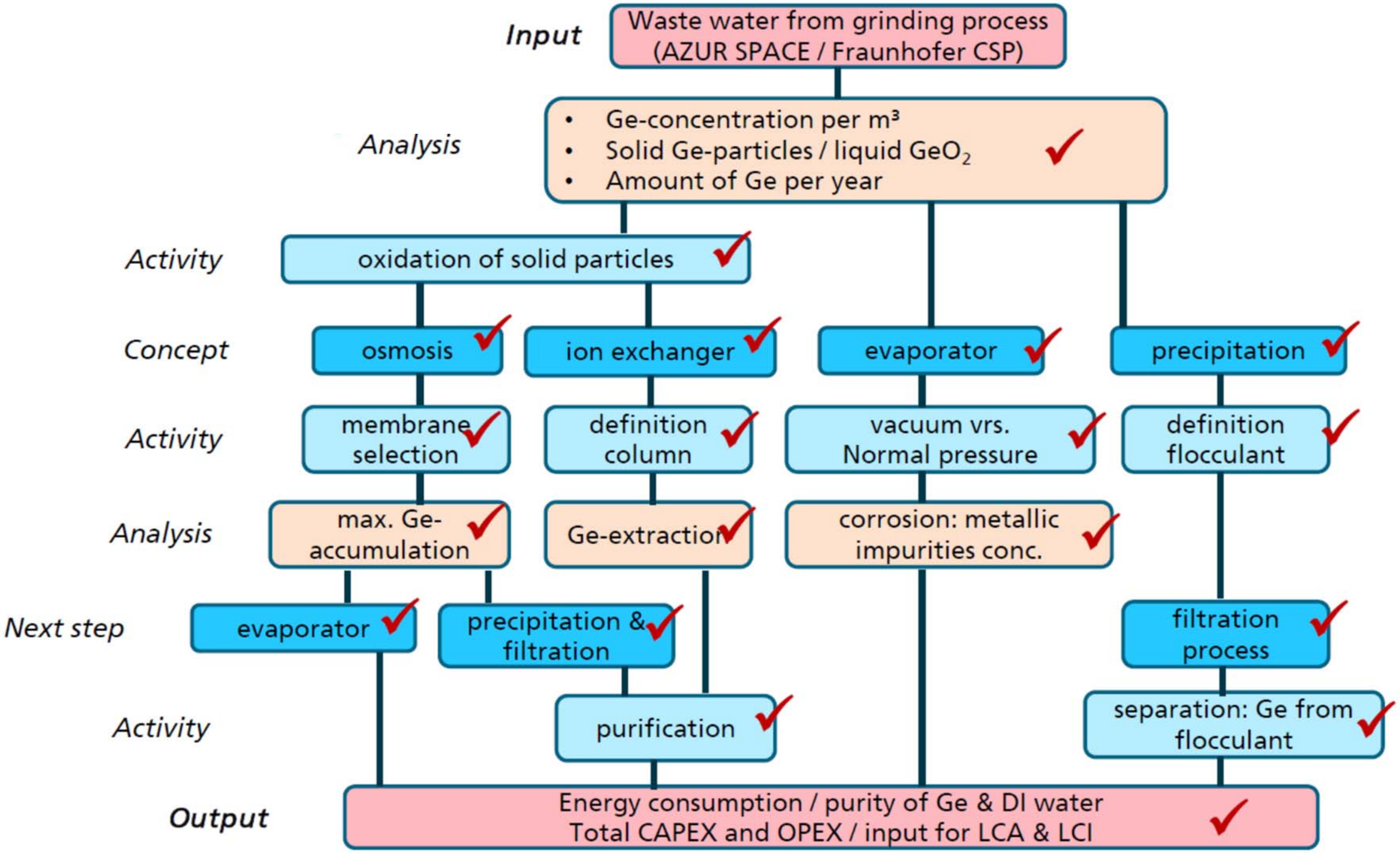
Ge Recovery from Grinding Slurry



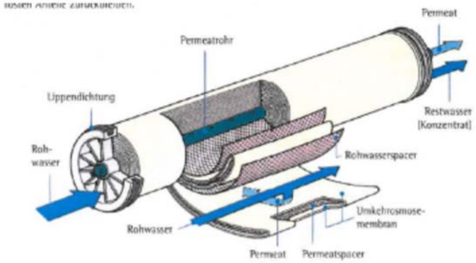
Ge Recovery from Grinding Slurry

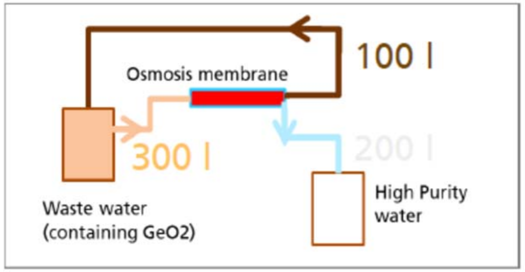
- **Evaporators:** Ge-concentration in the process water is too low; Vacuum evaporator are preferable for lower through-put; the low temperature bears less risk of solid deposits / crusts
- **Precipitation:** Extraction / de-complexation is laborious
- **Filtration:** only the solid particles are extracted, dissolved GeO_2 is lost
- **Osmosis:** accumulation of dissolved GeO_2 by a factor of 10 to 20 is easily (fast and at low energy consumption) possible; following step: evaporator
- **Ion-exchanger:** fast, low-cost solution with high extraction rates (>95 %); regeneration of resin externally

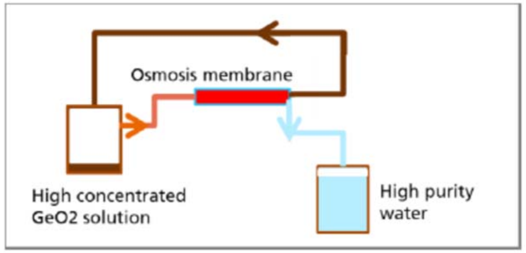
Ge Recovery from Grinding Slurry

Osmosis followed by Evaporation

- A membrane was connected to a water pump, flow meters and a 5 µm filter.
- The concentration in the concentrate increases by a factor of 2-3 with each cycle.





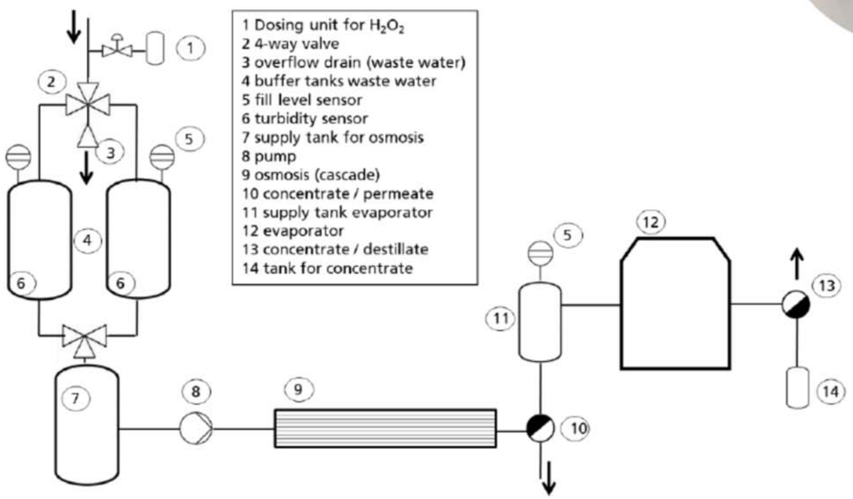


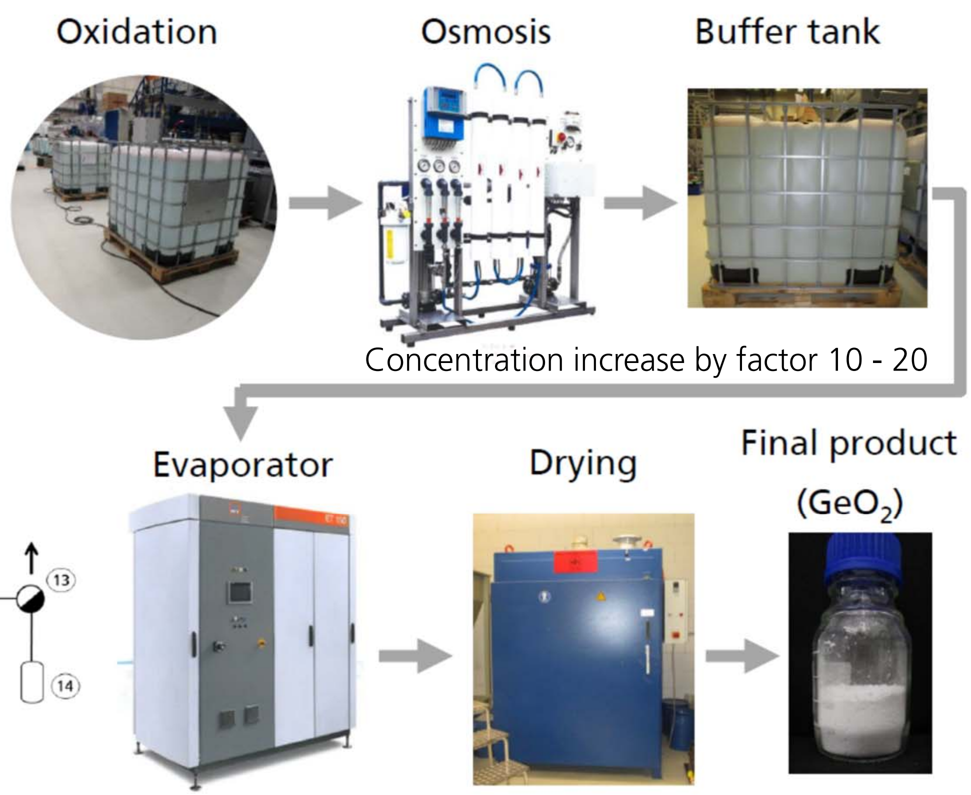
- In our case, 200 l/h high purity water / 100 l/h concentrate is obtained, i.e. about 4.5 h is needed for one IBC.

Ge Recovery from Grinding Slurry

Osmosis followed by Evaporation

- Capacity: > 1,000 liters/hour



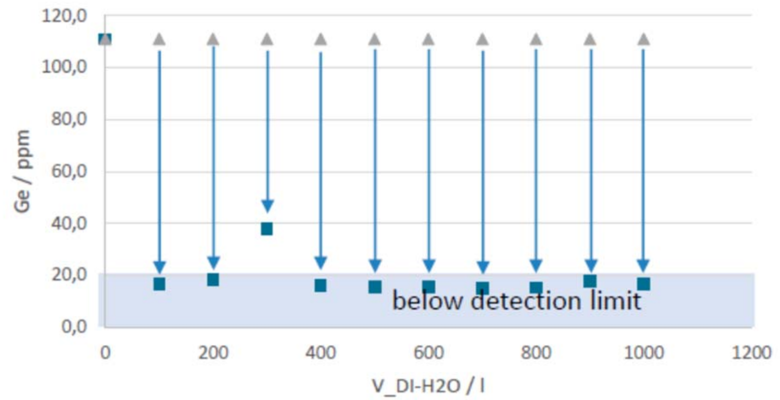


Ge Recovery from Grinding Slurry

Ion Exchange followed by Evaporation

- Test with an IBC of 1,000 liter with a GeO_2 concentration of 110 ppm, Flow rate: 300 l/h.
- Solid particles had been oxidized prior to the ion-exchanger using H_2O_2.
- Several ion-exchanger are now available at the CSP, the resin can be exchanged easily.
- Ge-concentration outlet: below detection limit (LOD=20ppm).
- A 20 l exchanger (which is still a rather small one) could extract 1 kg of germanium / could handle 10.000 liter of grinding water.

Ge-concentration in DI-H2O after passing the ion exchanger



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Ge Recovery from Grinding Slurry

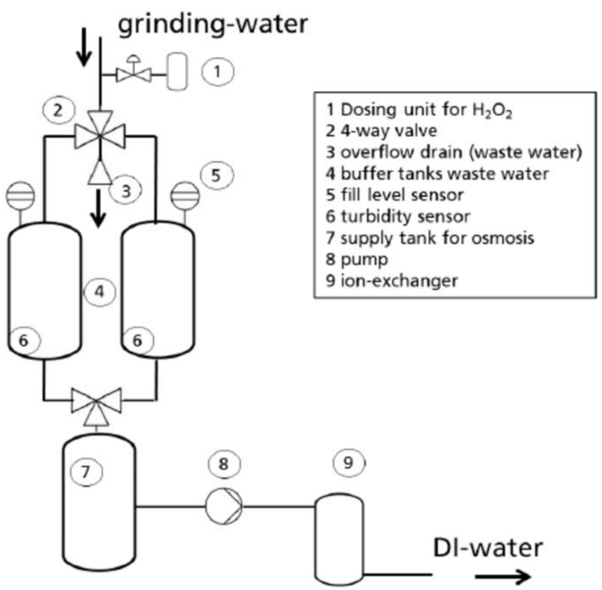
Ion Exchange followed by Evaporation

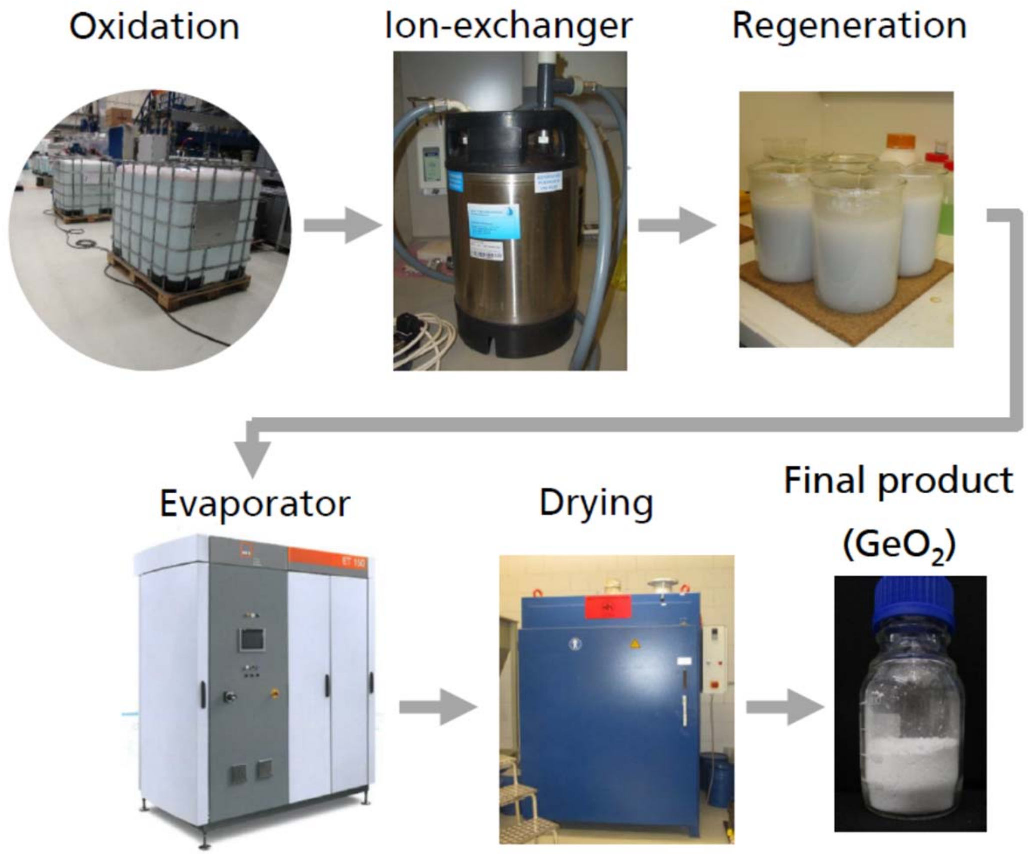
- For extraction, we used HCl. The acid solution was neutralized with NaOH and evaporated: GeO2 was recovered.
- With respect to energy consumption, an ion exchanger is very cheap (our pumps are driven by compressed air).

Ge Recovery from Grinding Slurry

Ion Exchange followed by Evaporation

- Capacity: 300 liters/hour
- Extraction rate >95 %





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Ge Recovery from Grinding Slurry

- Option 1: Filtration/Oxidation + Osmosis + evaporation + drying:
  DI-water + solid GeO_2
  - Osmosis: CAPEX and OPEX is low; evaporator: CAPEX and OPEX rather high
- Option 2: Filtration/Oxidation + Ion-exchanger + regeneration + evaporation + drying:
  wastewater + solid GeO_2
  - Ion-exchanger: CAPEX and OPEX is low; regeneration requires skills
- For low concentrated, high purity solutions, we recommend osmosis/evaporator or ion-exchanger; it might also depend, whether it is a continuous waste water stream or a batch application
- For low concentrated, low purity solutions, a first step filtration is recommended
- For high concentrated solutions, we go directly into the vacuum evaporator

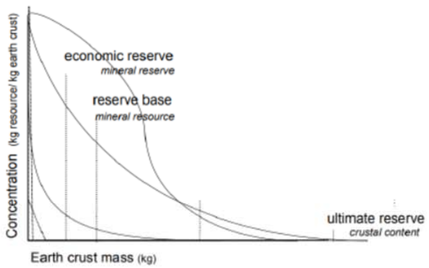
Ge Recovery from Grinding Slurry

LCA Analysis – Production of $GeCl_4$ from Secondary Ge

LCA analysis by A.A. Khan & S. Nold

Overview of Model Parameters	
Underlying Standard	ISO 14040-44
System Model	Cut-off (https://ecoinvent.org/the-ecoinvent-database/system-models/)
Model System Boundary	Cradle-to-gate
Geographical System Boundary	DE: market for electricity, medium voltage (Germany)
Software Used	Umberto 11
Data Source for Life Cycle Inventory	Ecoinvent v3.8 (background)

LCIA Category	LCIA Method	Unit
Global Warming Potential	IPCC 2013 100y	kg CO2 eq
Ozone Depletion Potential	CML (ReCiPe 2008)	kg CFC-11 eq
Particulate Matter	ReCiPe 2008	kg PM10 eq
Acidification	CML 2001 (2016)	kg SO2 eq
Freshwater Eutrophication	ReCiPe 2008	kg P eq
Marine Eutrophication	ReCiPe 2008	kg N eq
Ionising Radiation	ReCiPe 2008	kBq U235 eq
Photochemical Oxidant Formation	ReCiPe 2008	kg NMVOC eq
Minerals and Metals Resource Depletion, Ultimate Reserve	CML (Environmental Footprint 3)	kg SB eq
Fossil Resource Depletion	ILCD 2011 (CML Environmental Footprint 3)	MJ
Freshwater Ecotoxicity	UseTox	CTUe
Marine Ecotoxicity Potential	CML 2001 (2016)	kg 1,4-DCB eq
Human Toxicity, Cancer	UseTox	CTuh
Human Toxicity, Non-Cancer	UseTox	CTuh
Gross Water Consumption	Environmental Footprint 3	m3 world eq
Primary Energy Consumption	CED	MJ



- Reserve base, corrected,
- Reserve base, uncorrected
- Ultimate reserve

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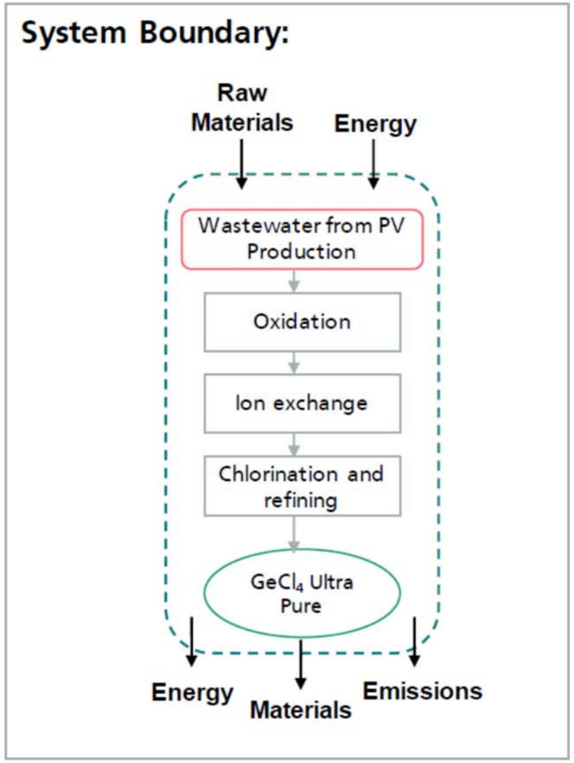
Ge Recovery from Grinding Slurry

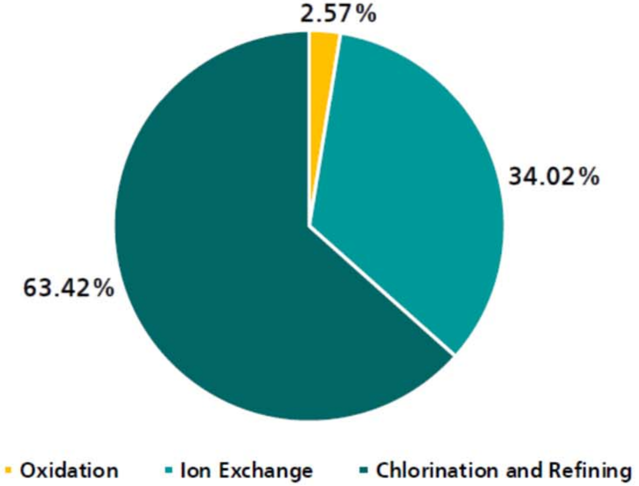
LCA Analysis – Production of $GeCl_4$ from Secondary Ge - „Ion Exchange & Evaporation“



Functional Unit: This study is a cradle to gate LCA of 1 kg ultrapure germanium tetrachloride ($GeCl_4$) produced from secondary germanium obtained from grinding wastewater from PV production.

Total Global Warming Potential (GWP): 29.69 kg CO_2-Eq./ kg ultrapure $GeCl_4$

Process Contribution in Impacts:



Ge Recovery from Grinding Slurry

LCA Analysis – Production of $GeCl_4$ from Secondary Ge - „Ion Exchange & Evaporation"

Global Warming Potential (GWP) – Hotspot analysis

Recycling Steps	GWP (kg CO_2-Eq/kg $GeCl_4$)
Oxidation	**0.76**
electricity, medium voltage	0.50
hydrogen peroxide production, product in 50% solution state	0.27
Ion Exchange	**10.10**
electricity, medium voltage	1.50
hydrochloric acid, without water, in 30% solution state	0.62
sodium hydroxide, without water, in 50% solution state	0.49
wastewater from PV cell production	7.48
water, deionised	0.01
Chlorination and Refining	**18.83**
electricity, medium voltage	0.98
hydrochloric acid, without water, in 30% solution state	17.84
wastewater from PV cell production	3.04E-03
Total GWP	**29.69**

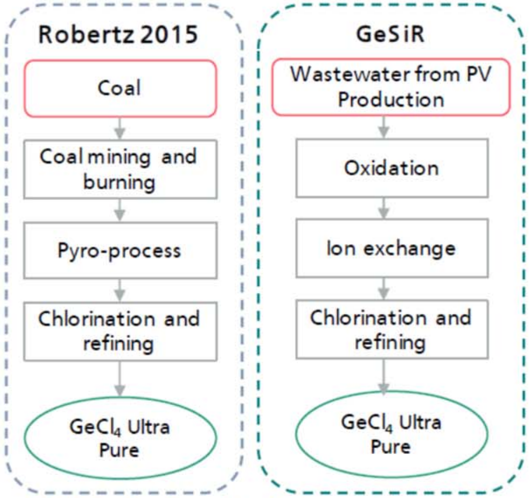
Analysis of result:

- The most contributing recycling step is *Chlorination and Refining*, followed by *Ion Exchange* step. The step *Oxidation* showed the least impacts.
- The highest contributing material to produce ultra pure $GeCl_4$ from secondary Ge is the HCl used in chlorination and refining.
  - ~31kg HCl is needed to produce 1kg $GeCl_4$
- Second highest contributing input is the wastewater from PV production due the large volume requirement.
  - Based on the LCI, 1 kg of Ge is present in 10000 liters of wastewater.
- Third highest input contributing to the GWP is the electricity consumed in the ion exchange process.

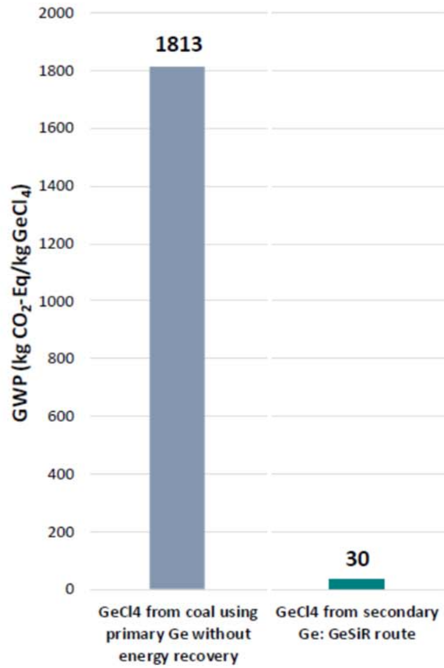
Ge Recovery from Grinding Slurry

LCA Analysis – Production of $GeCl_4$ from Secondary Ge – „Ion Exchange & Evaporation"

Global Warming Potential (GWP) – Comparison



- *Robertz (2015):* Production of $GeCl_4$ from coal using primary Ge via the pyrometallurgical route with and without energy recovery.
- *GeSiR Route:* Production of $GeCl_4$ from grinding wastewater from PV production using primary and secondary Ge.



Route 1, 2 and 3 sourced from Robertz, B., Verhelle, J. and Schurmans, M. (2015) The Primary and Secondary Production of Germanium: A Life-Cycle Assessment of Different Process Alternatives, JOM, 67, 412-424. https://doi.org/10.1007/s11837-014-1267-6
Database: GaBi and ELCD; Evaluation Method: ILCD by Environmental Footprint
Database: Ecoinvent 3.8; Evaluation Method: IPCC 2013

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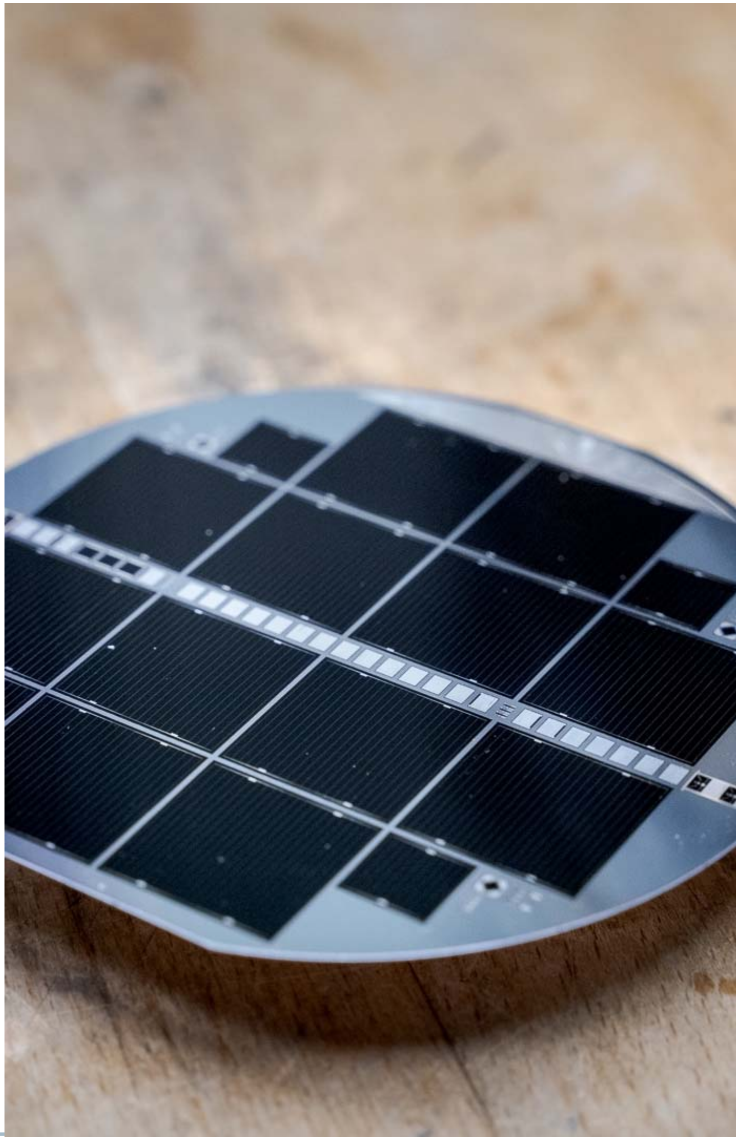
Ge Recovery from Grinding Slurry

Summary

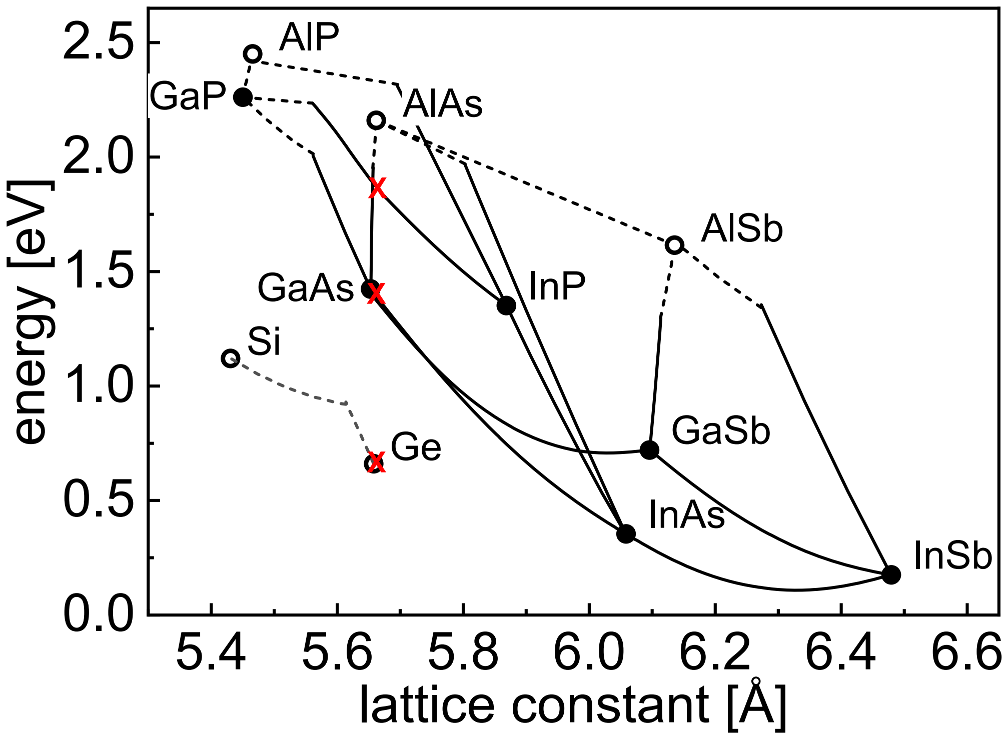
- **> 95% recovery of germanium from grinding wastewater is relatively easy and can be done in an economical way.**
- 30 kg CO_2-Eq. is emitted per kg of ultrapure $GeCl_4$ production from secondary germanium sourced from grinding wastewater. The impact is are **61 times lower** compared to $GeCl_4$ from primary germanium produced from coal ash without energy recovery

Content

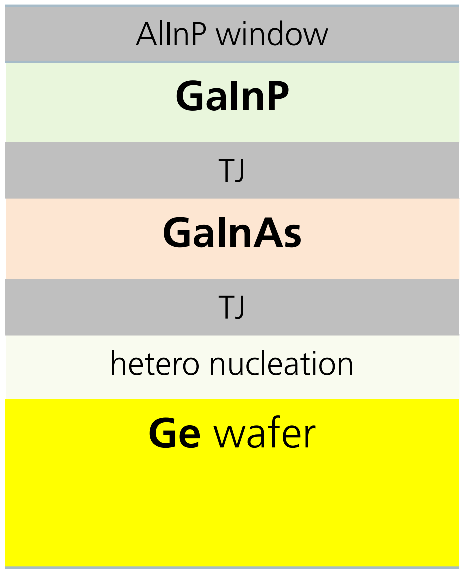


Low Ge Alternative Triple Junction

Motivation



„standard“ lattice matched 3J



Low Ge Alternative Triple Junction

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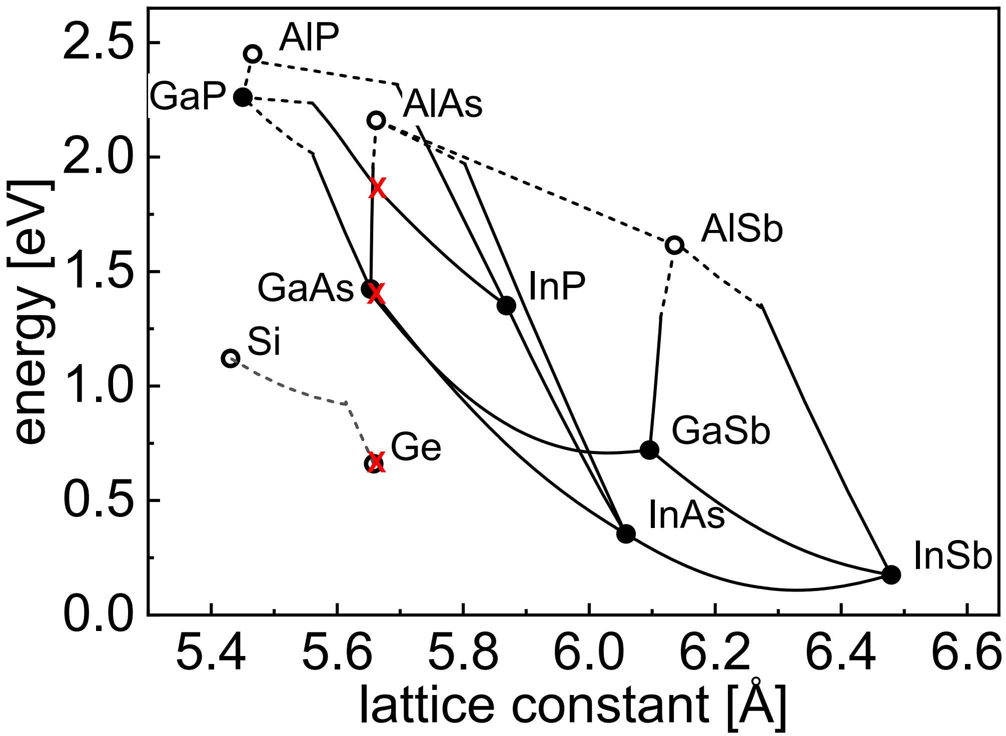
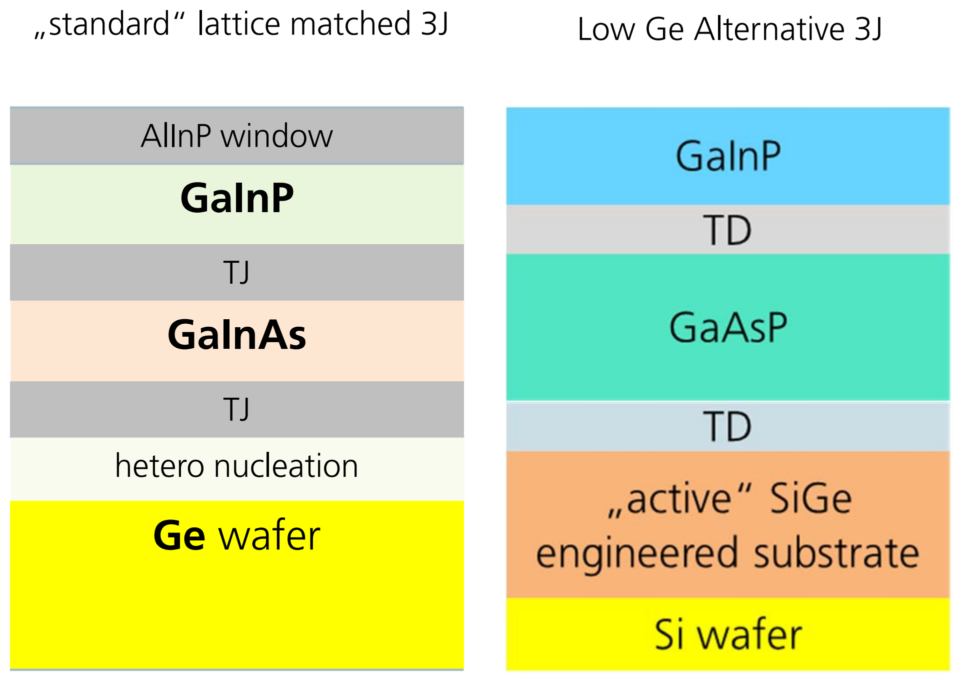
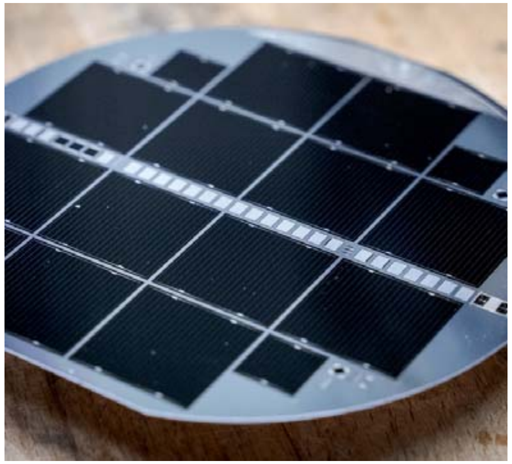




Low Ge Alternative Triple Junction



2 cm x 2 cm mask used for solar cell processing

Based on existing dual–junction solar cells

4" „engineered substrate" from US supplier with specific SiGe absorber design (according to initial simulations)

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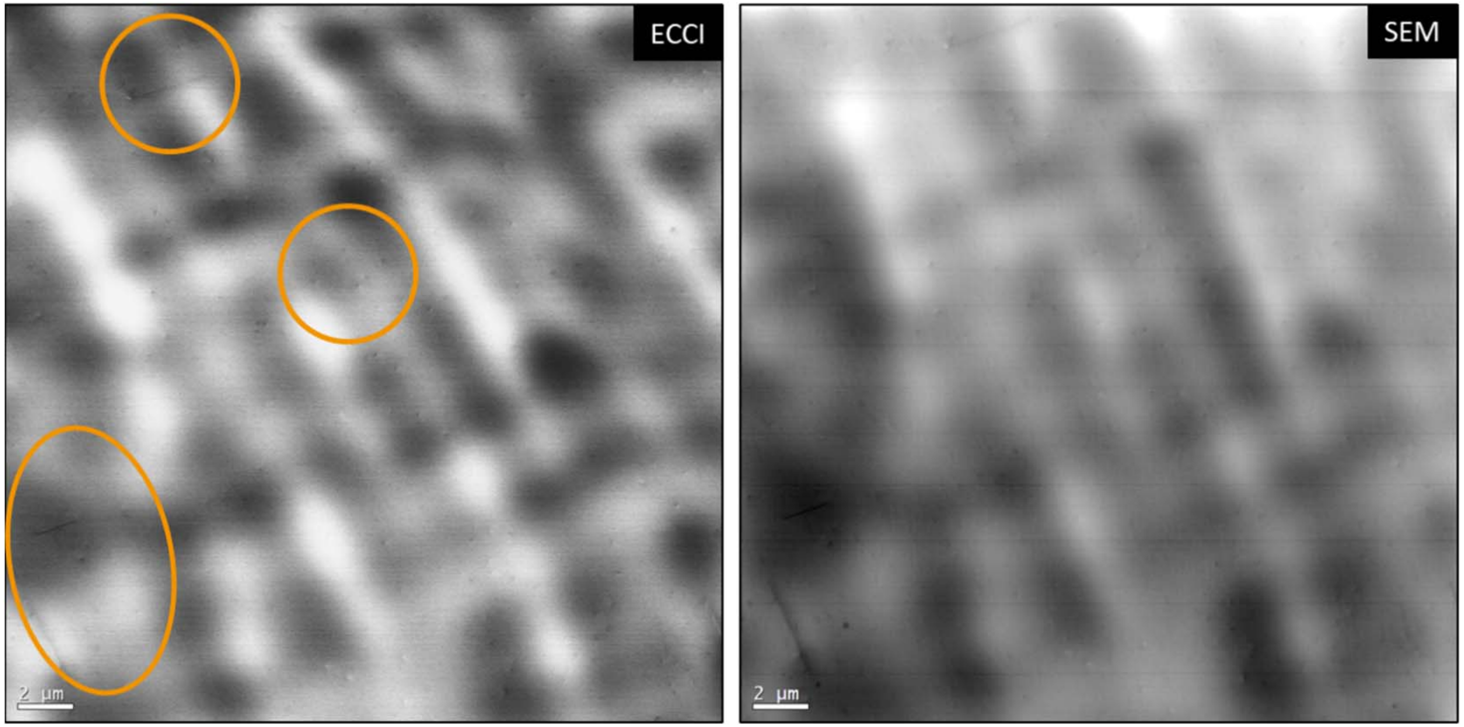
Low Ge Alternative Triple Junction

SiGe Engineered Substrates

ECCI analysis before III-V epitaxy

- Misfits visible on surface
- TDD: $2.7*10^{7}$ cm^{-2}
- TDD expectation:< $3*10^{6}$ cm^{-2}

ECCI



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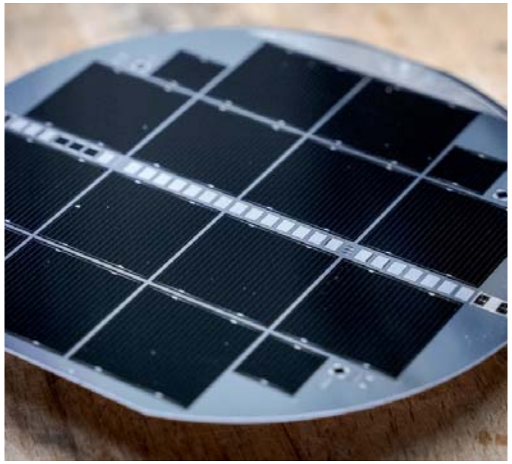

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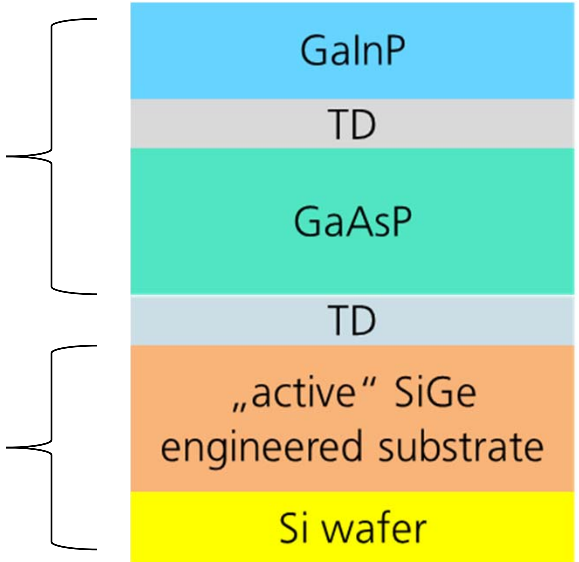
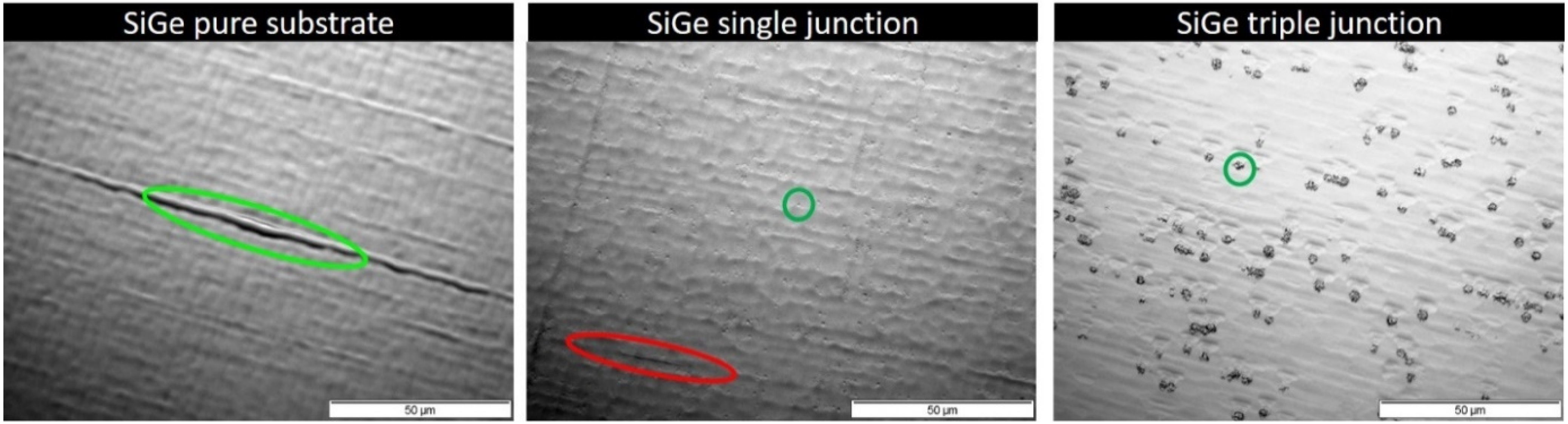


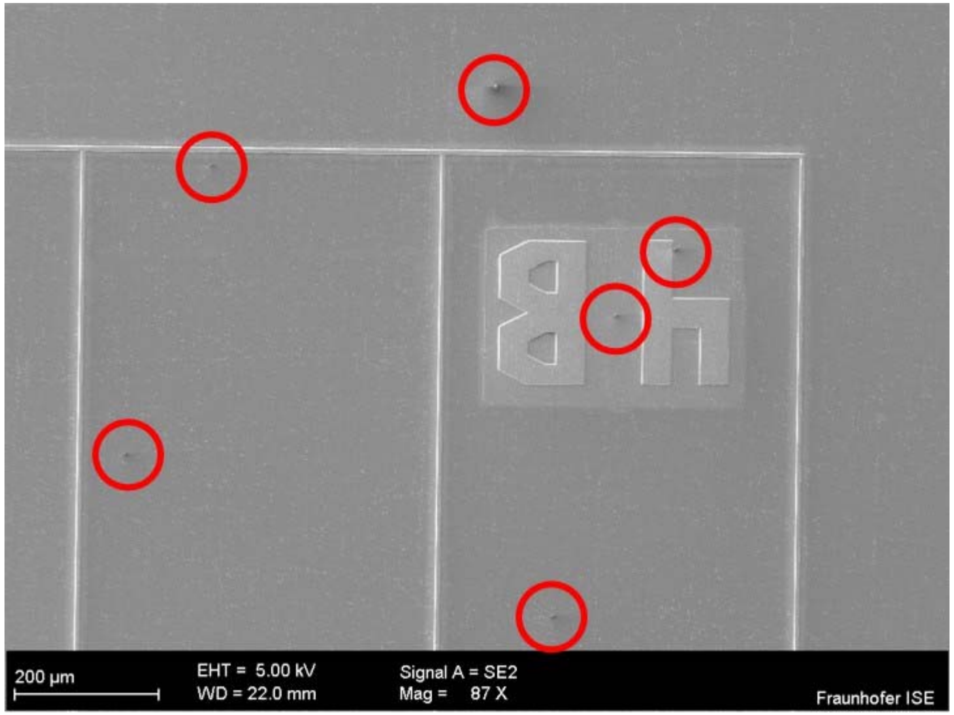
Low Ge Alternative Triple Junction

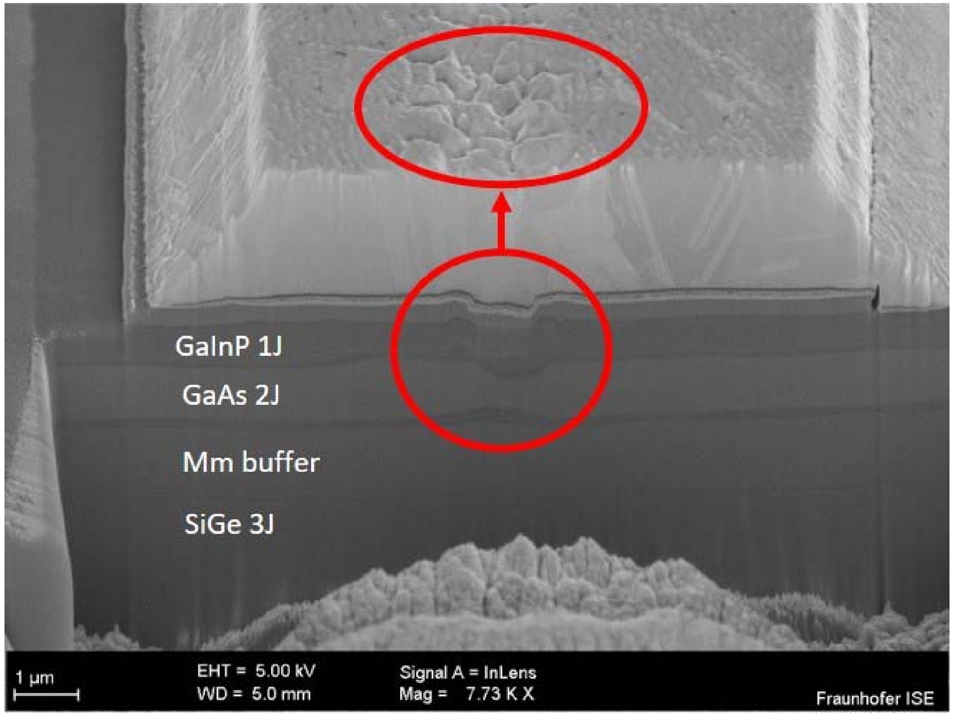
SEM Images of Wafer Surface after Epitaxy



Low Ge Alternative Triple Junction

SEM Images of Processed Devices





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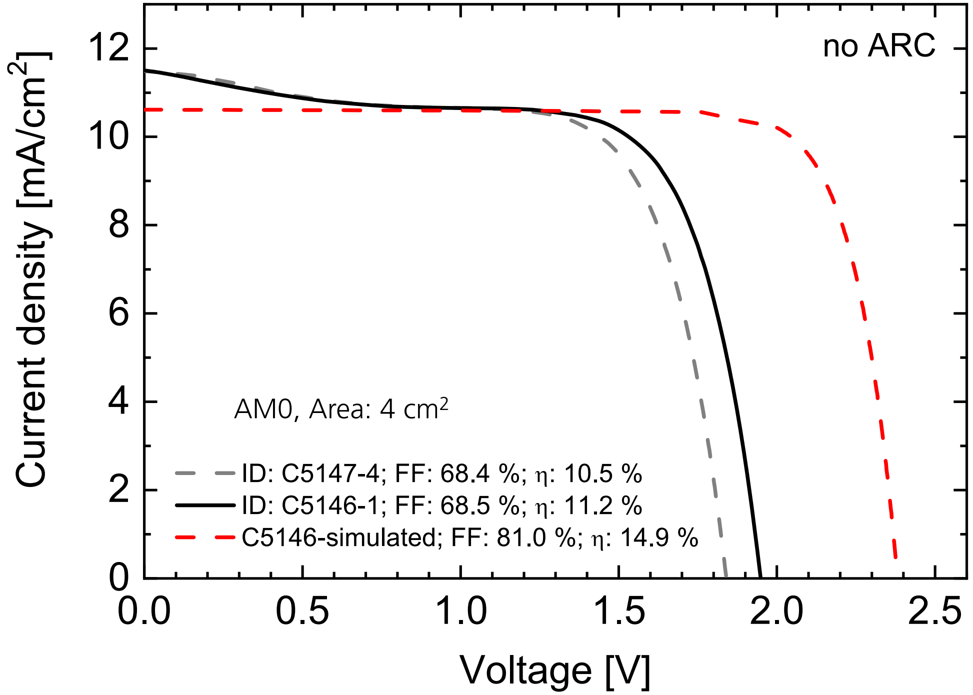
Low Ge Alternative Triple Junction

GaInP/GaAsP/SiGe Triple-Junction

I-V under illumination of triple junction cell



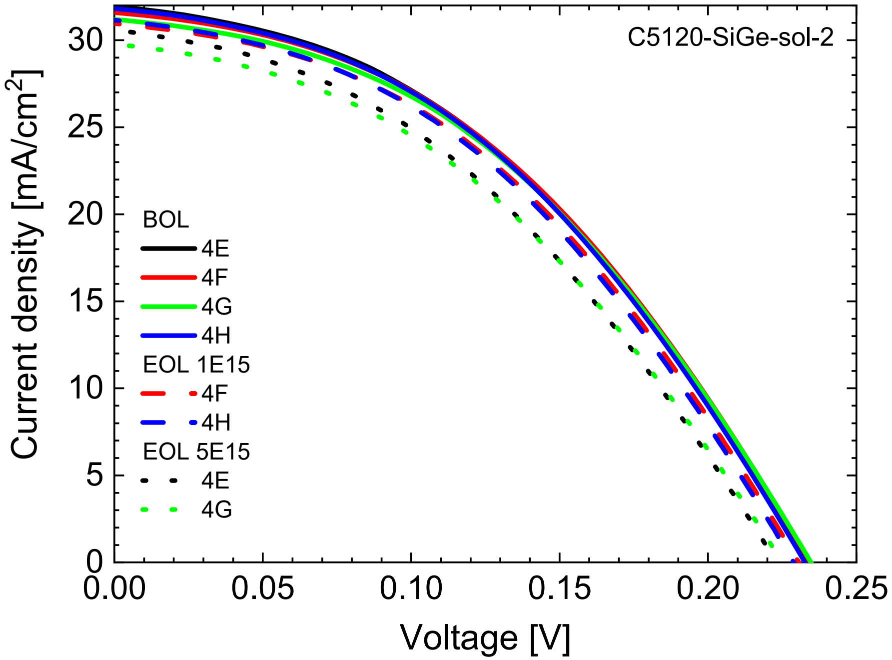
a)

b)

Low Ge Alternative Triple Junction

1 MeV Electron Irradiation

I-V under illumination of single junction SiGe cell for differnent fluences of 1 MeV electron irradiation

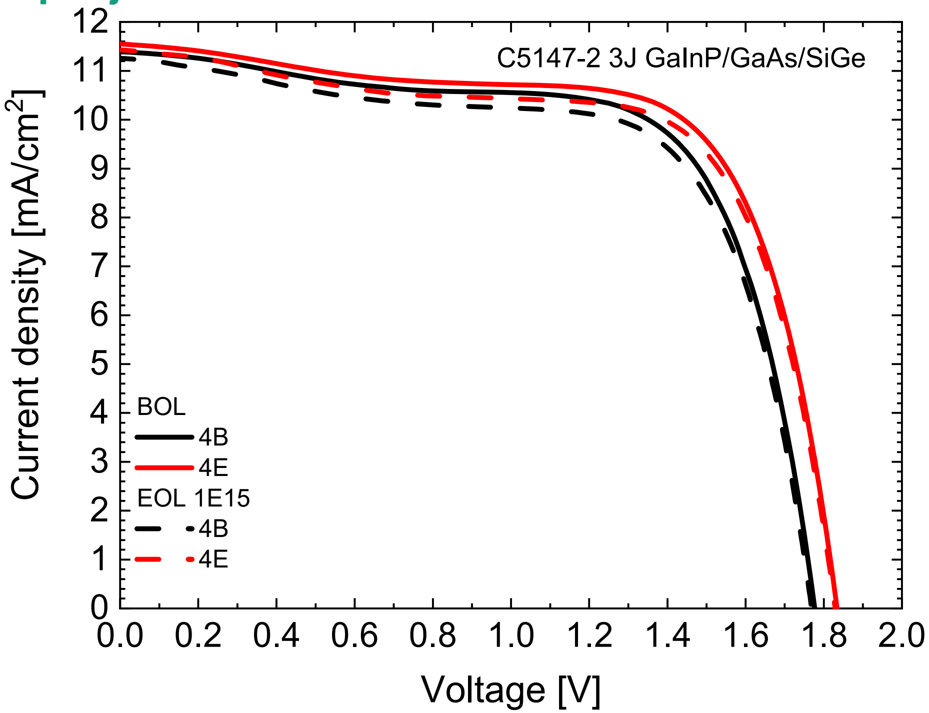


a) b)

Low Ge Alternative Triple Junction

1 MeV Electron Irradiation

I-V under illumination of triple junction cell for $1*10^{15}$ cm^2 1 MeV electron irradiation



→ due to high threading dislocation density, small effect of irradiation for current devices a)

b)

Low Ge Alternative Triple Junction

Engineering Tests – Thermal Cycling

1. a dip in liquid Nitrogen (LN Dip)

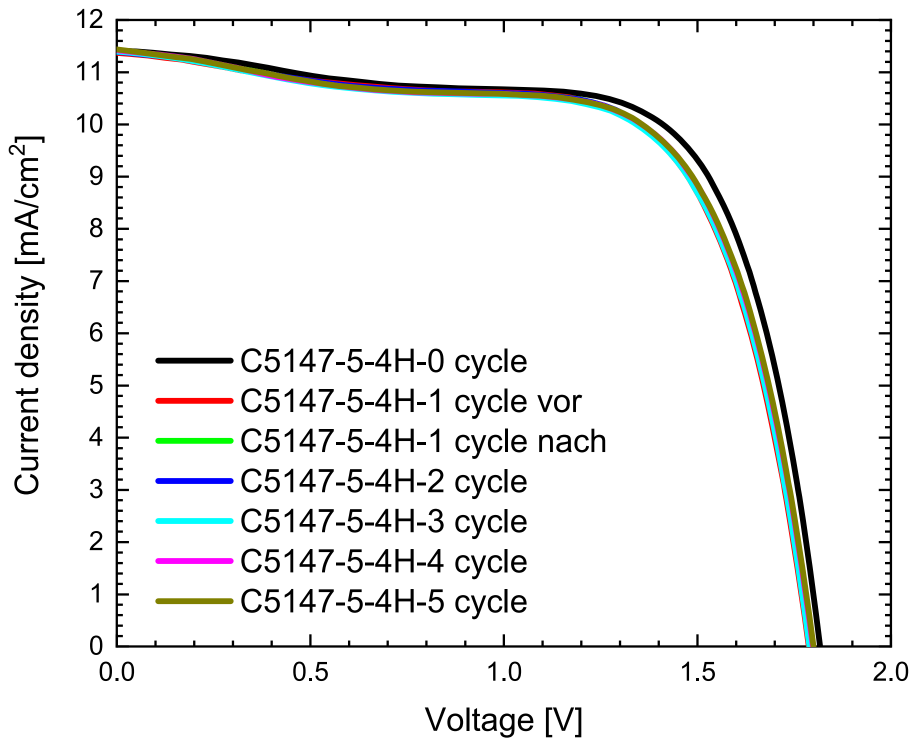
2. a heat up to room temperature (RT)

3. waiting for 5 min on the sample chuck at RT

4. heating to 50°C on the chuck and waiting for 5 min

5. cool down to RT and waiting on the sample chuck

6. IV measurement at RT on the sample chuck



→ No degradation after 5 cycles

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Low Ge Alternative Triple Junction

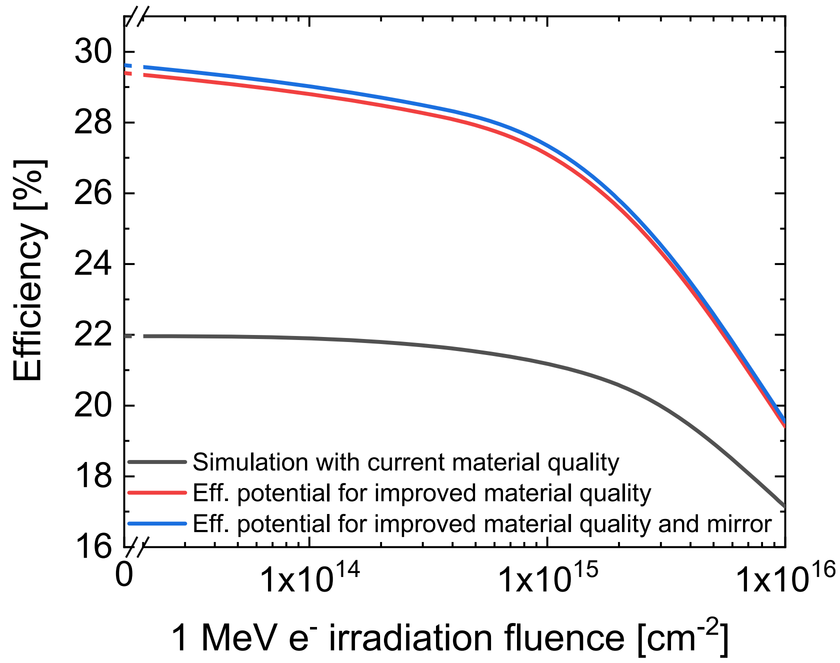
Product Development Roadmap

1. **SiGe metamorphic buffer and SiGe epitaxy (6 yrs)**

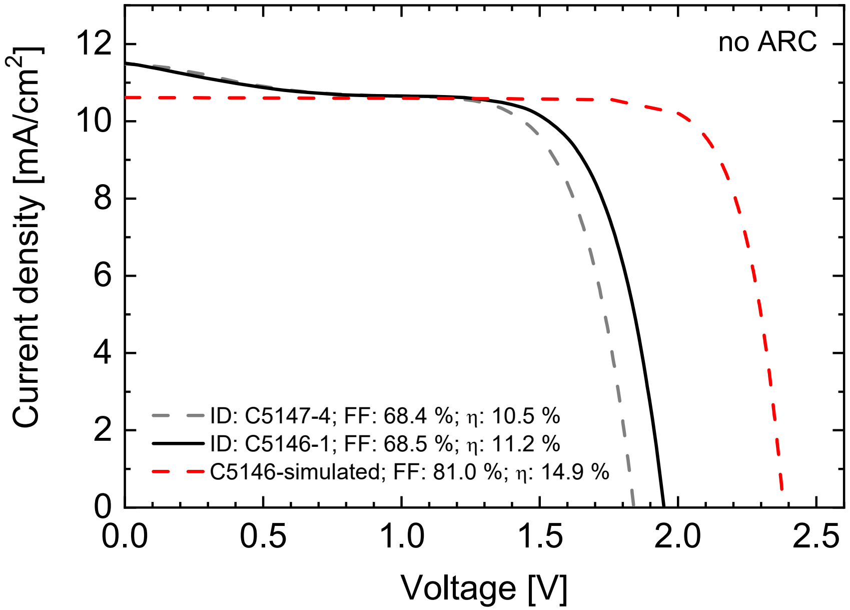
2. **Triple-Junction & III-V epitaxy Development (2-4 yrs)**

3. **Industrialization & Space Qualifications (3-5 yrs)**

Performance estimation



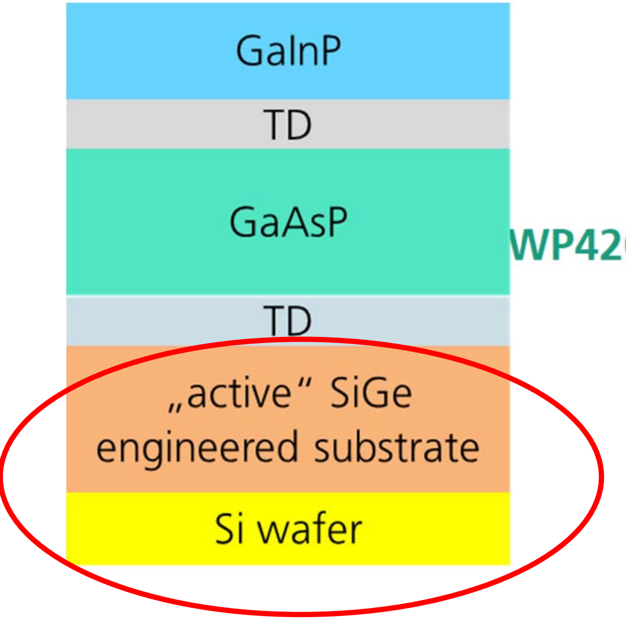
Low Ge Alternative Triple Junction
Summary



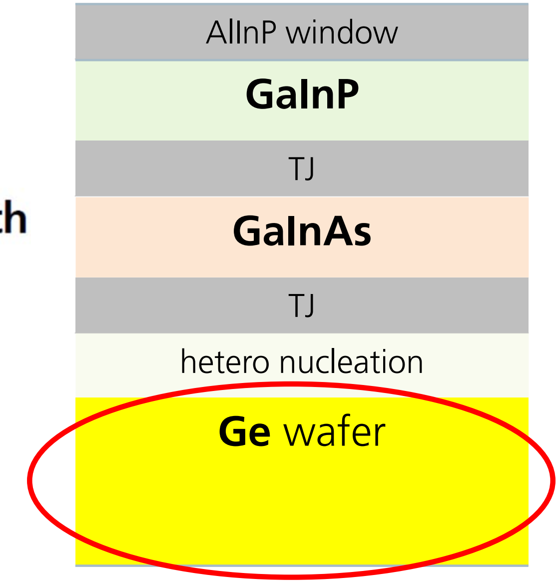
→ Successful demonstration of first GaInP/GaAsP/SiGe triple junction cell as “low Ge alternative”

Low Ge Alternative Triple Junction

LCA Analysis



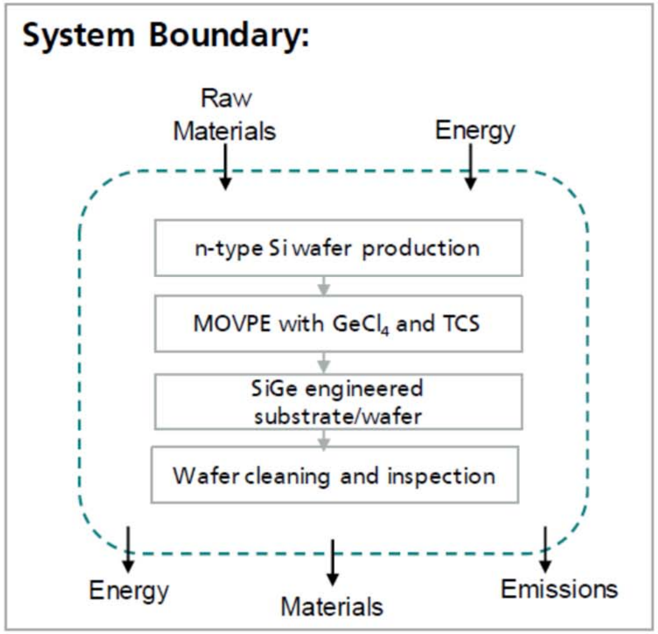
WP420 – Comparison of LCA of 200µm Ge-wafer with 5 µm SiGe substrate on 150 µm Si-wafer

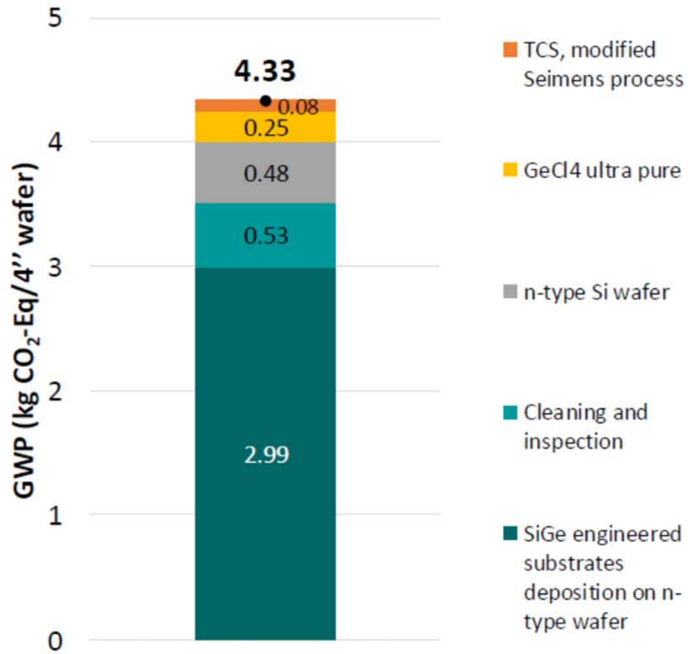


SiGe Engineered Wafer - LCA Analysis

4“ SiGe on Si

This study is a cradle to gate LCA of one 4“ SiGe engineered substrate on Si. The primary Ge is obtained from lead mining





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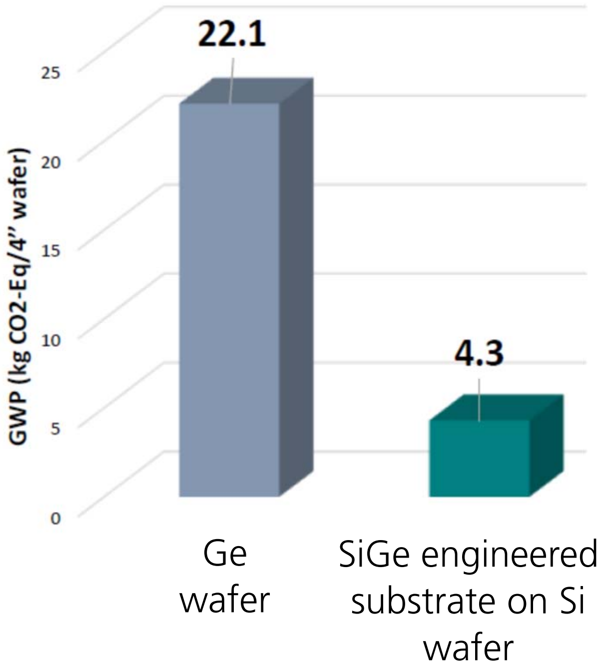
SiGe Engineered Wafer - LCA Analysis

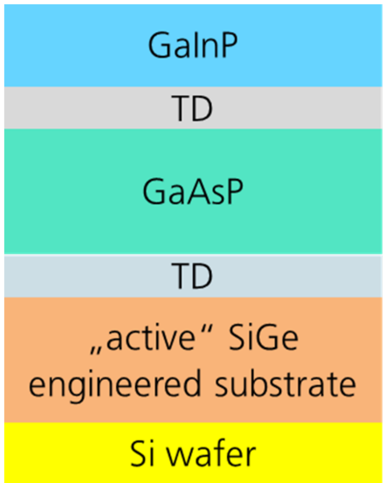
Comparison 4" Wafers

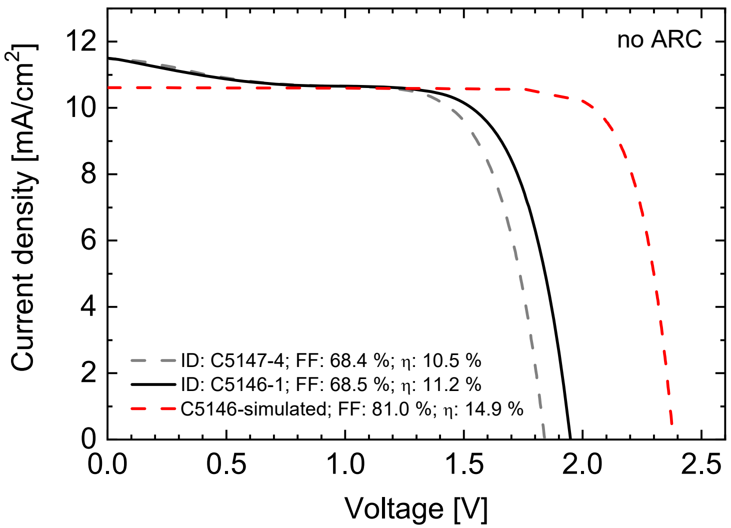


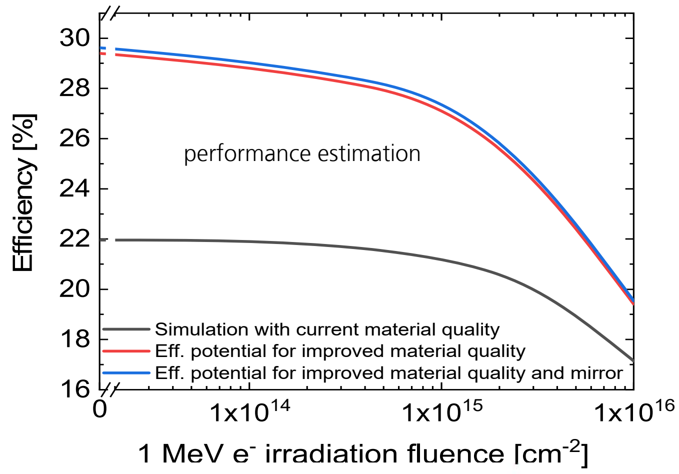
- SiGe engineered substrate: 5 times lower GWP than Ge wafer
- 18 times less primary Ge consumpotion

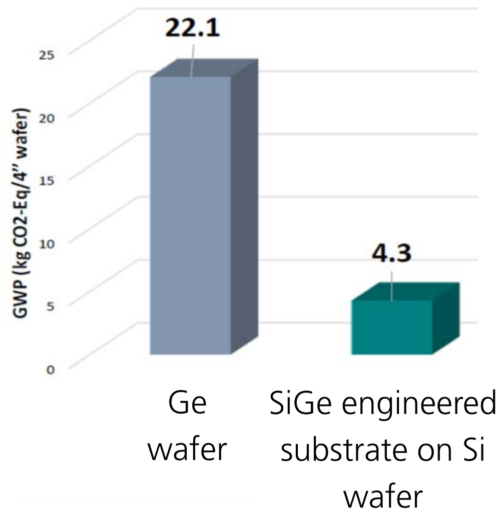
Low Ge Alternative Triple Junction

Summary









→ **Successful demonstration of first GaInP/GaAsP/SiGe triple junction cell as “low Ge alternative”**
→ **Efficiency potential similar to todays 3J on Ge → 18 times lower Ge consumption**

Thank you for your Attention!

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Kontakt

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