ULB UNIVERSITÉ LIBRE DE BRUXELLES

CHARACTERIZATION SYNTHESIS 4MAT RECYCLING ENGINEERING

ECOLE POLYTECHNIQUE DE BRUXELLES

ISSUES AND LIMITATIONS OF RECYCLING – THE CASE OF GALLIUM

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4MAT DEPARTMENT AT ULB

- 4MAT = characterization, synthesis, processing & recycling

Marie-Paule Delplancke	Marc Degrez	Stéphane Godet
		

- Marc Degrez's team:
  - Study of recycling processes
  - Life cycle assessment
  - Process improvement

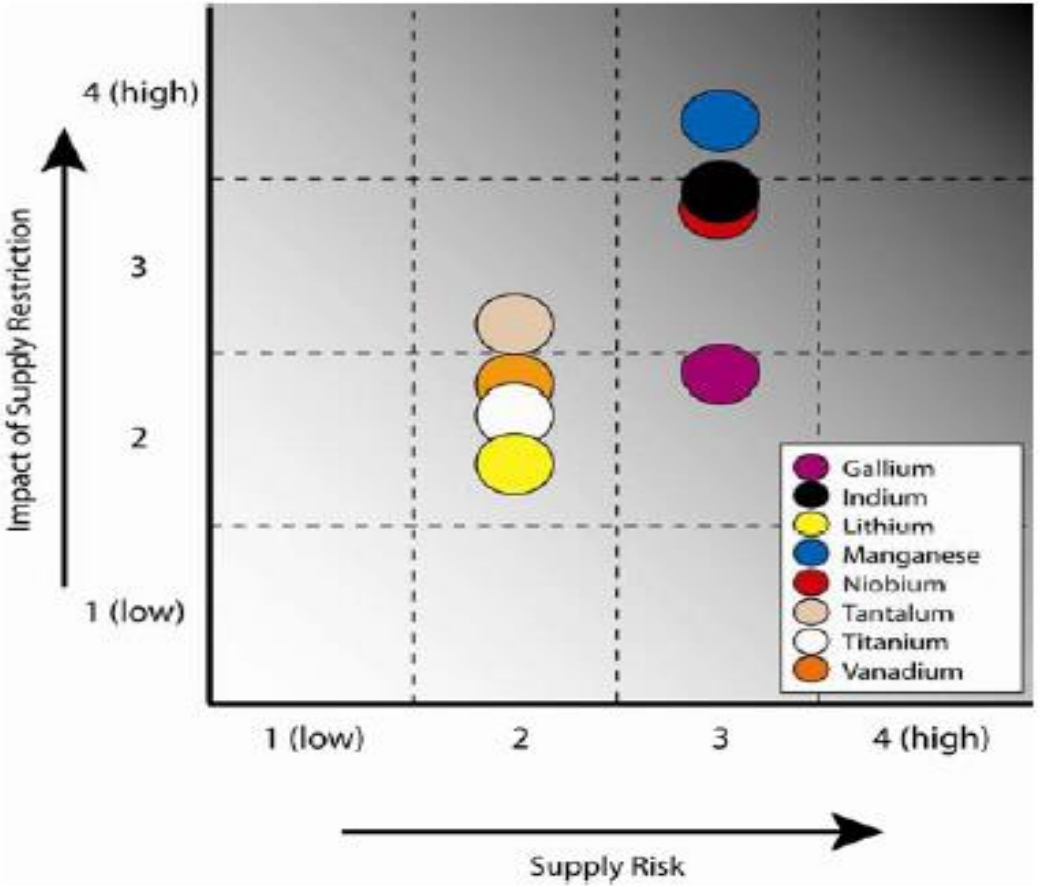
Roadmap

- Supply risk and scarcity
- Demand & applications
- Primary production:
  - Offer
  - Processes
  - Environmental aspect
- Secondary production:
  - Available waste
  - Current practice
  - Obstacles
- Solutions?

SUPPLY RISK AND SCARCITY

- Point of view of the NRC

What happens if gallium is not provided?

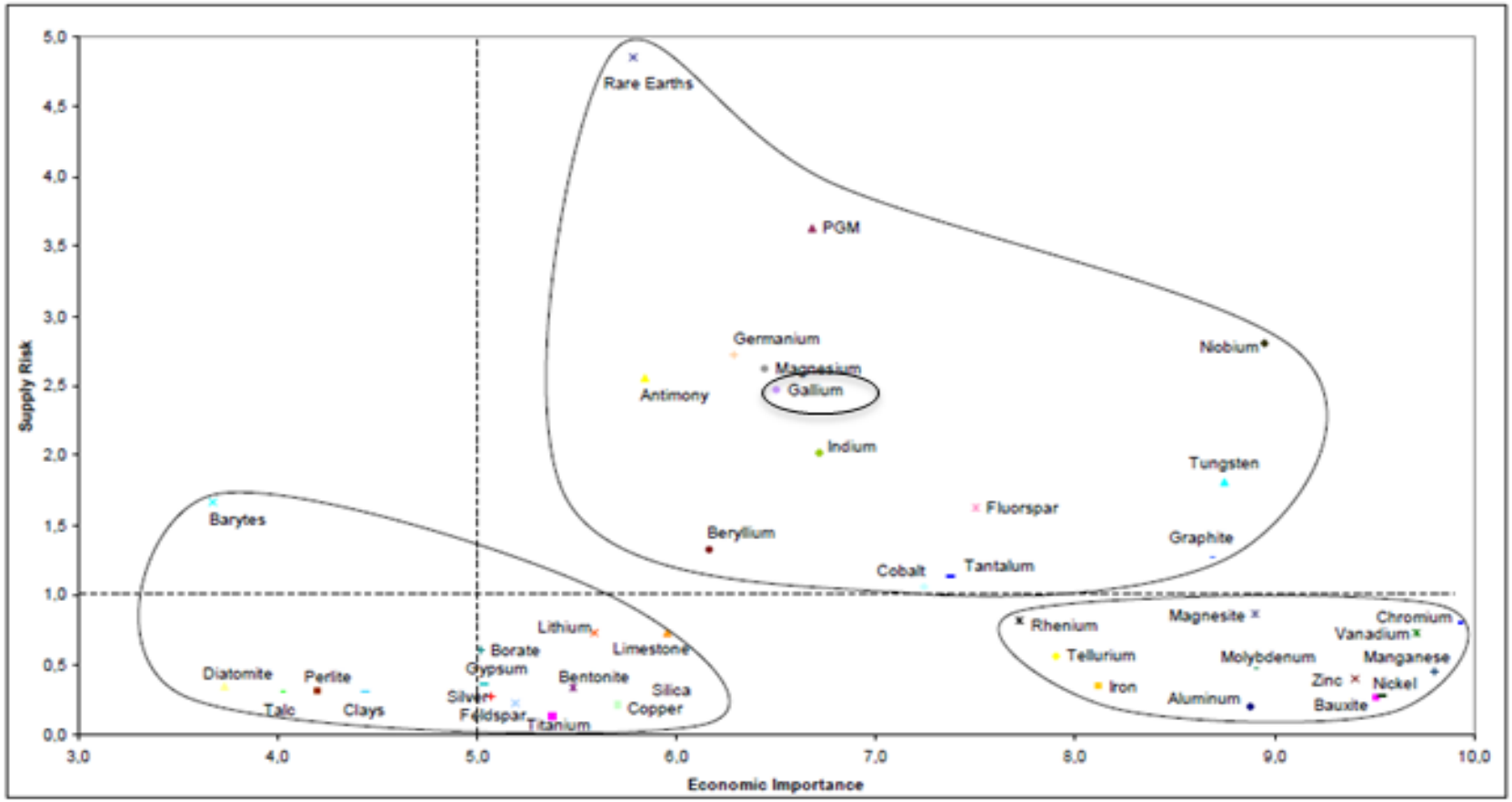


Is it available?
(short, long term)

NATIONAL RESEARCH COUNCIL (NRC) (2007), *Minerals, Critical Minerals, and the U.S. Economy*, Washington, DC : The National Academies Press

SUPPLY RISK AND SCARCITY

- Point of view of the EC

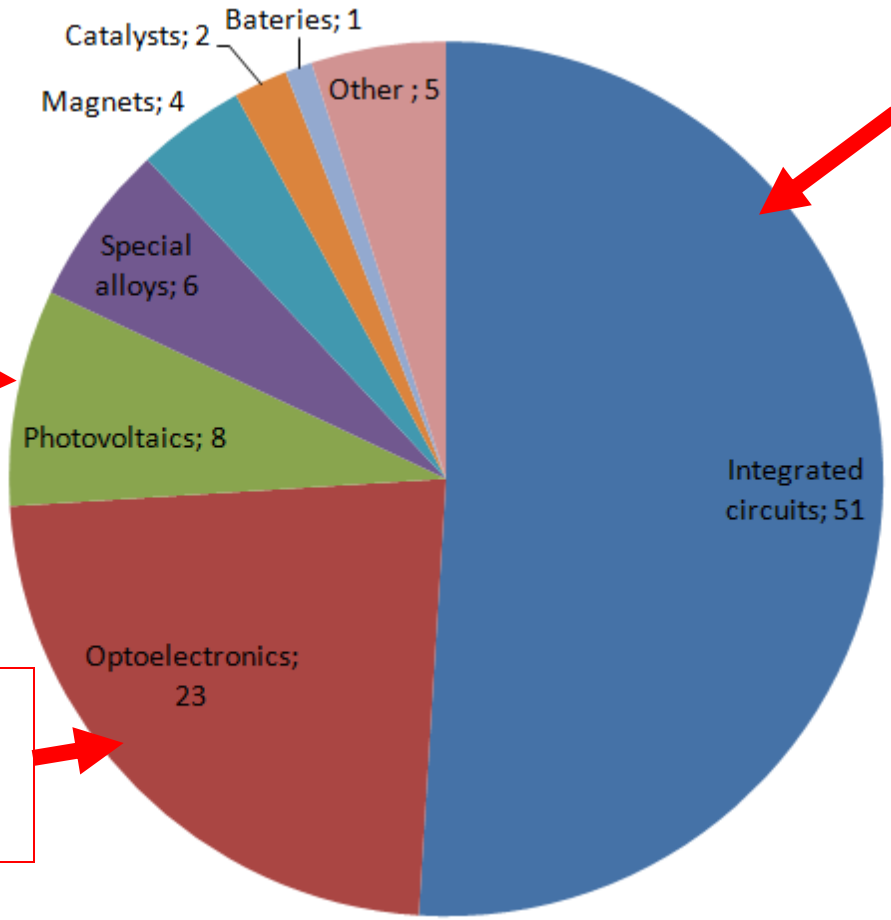


- No European (or World) project of Ga recycling in consumers goods

EUROPEAN COMMISSION ENTERPRISE AND INDUSTRY (ECEI) (2010a), *Critical raw materials for the EU : Report of the Ad-hoc Working Group on defining critical raw materials*, European Commission.

Demand & applications

- Overview



GaAs:
Cell phones
Radars
Satellite
…

Fast growing
Cu-Ga-In-Se

GaAs, GaN, GaP, GaSb:
Diodes (LED)
Laser diodes

ROSKILL (2011), *Gallium : Global Industry Markets and Outlook : Eighth edition*, Roskill Information Services, 108 p.

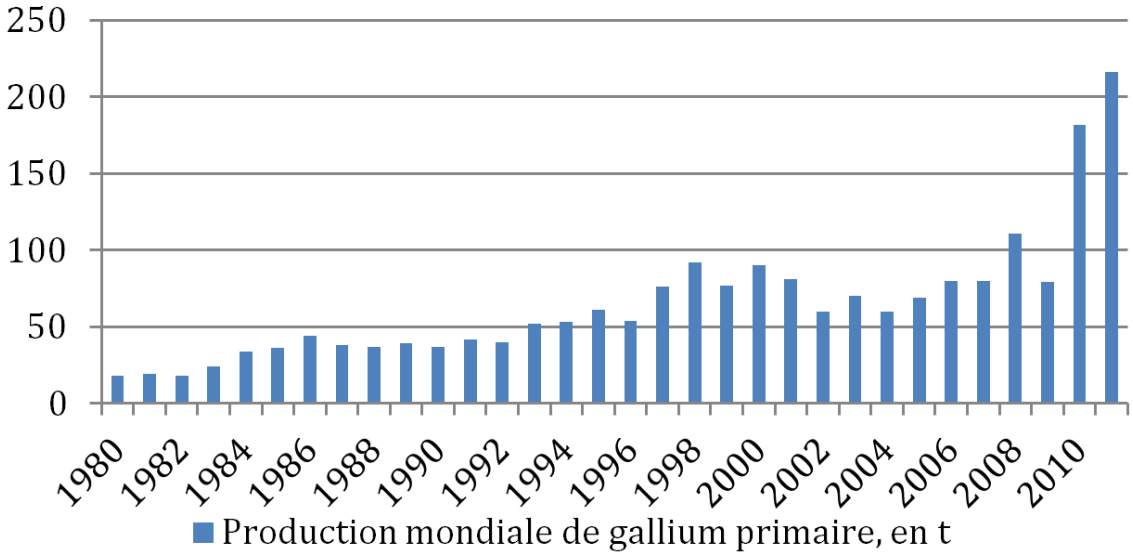
Demand & applications

- Ga can be considered as « critical »
- → Is secondary production able to mitigate the problem?

- Needed for emerging technologies
- → Increased permissivity for Ga primary production?

PRIMARY PRODUCTION

- Abundance: 19 ppm
- No profitable ore
- Extracted as a byproduct of Al and Zn production
- Bauxite:
  - ~50 ppm
  - > 1 MT available
- World production:



- BERSANI François (s.d.), *Métaux stratégiques : La France s'organise*, Bureau de Recherches Géologiques et Minières (BRGM)
- US Geological Survey (USGS) (2011a), *Mineral Commodity Summaries : Gallium*, rédigé par JASKULA Brian W., pp. 58-59

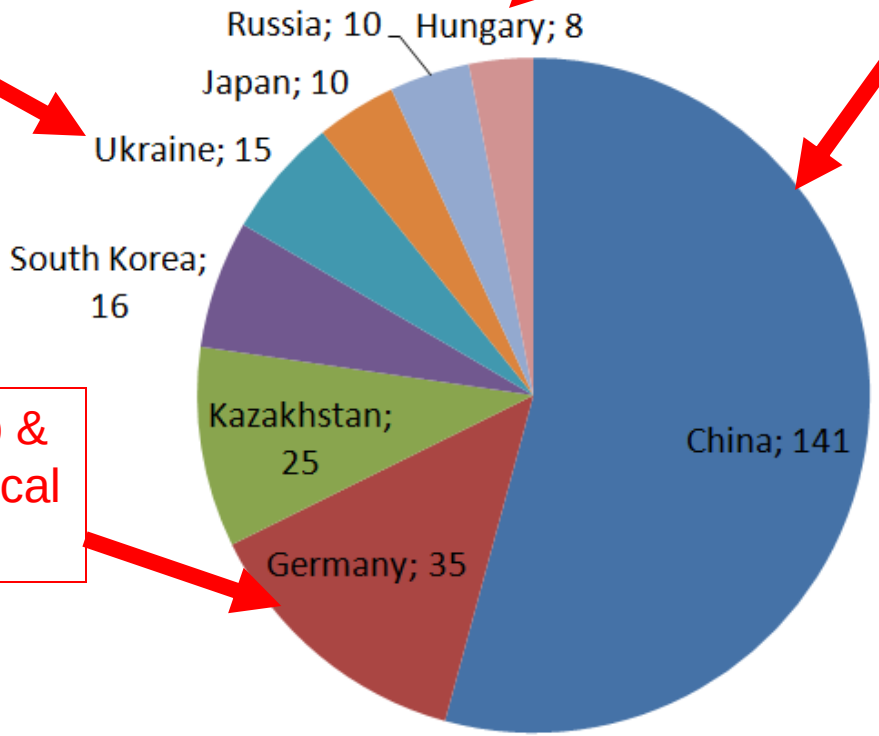
PRIMARY PRODUCTION

- World capacity:
  - Total: 260 T
  - Effective production: 201-212 T
  - Recent reduction of the difference

MAL Hungarian Aluminium Ltd

Sharp increase!

RUSAL

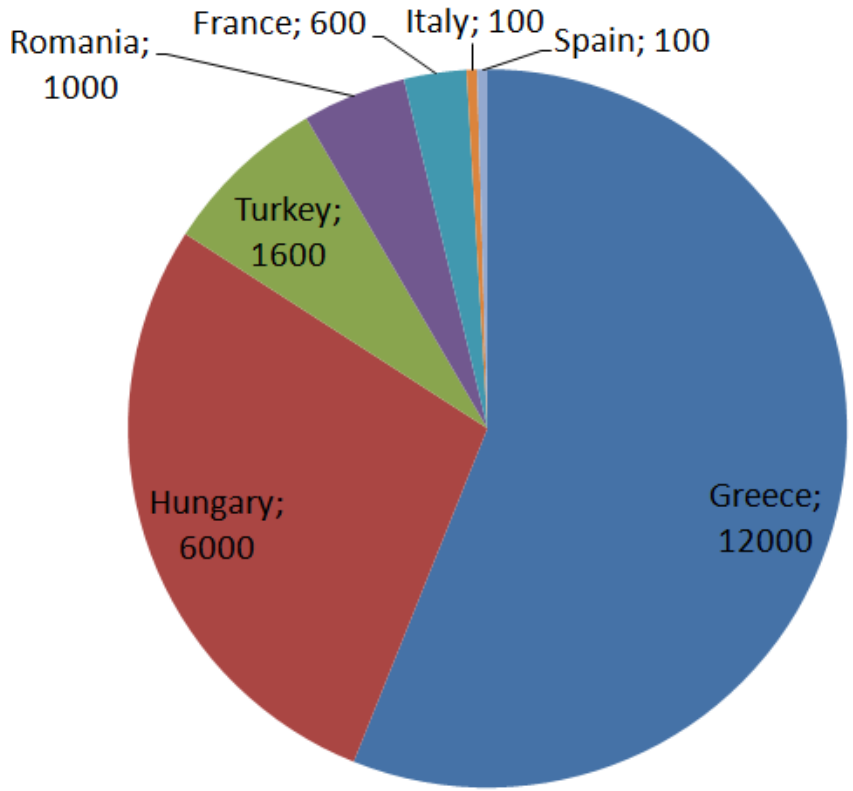


Ingal-Stade (Molycorp & MCP): hydrometallurgical production

US Geological Survey (USGS) (2012b), *2010 Minerals Yearbook : Gallium*, rédigé par JASKULA Brian W., USGS, 7 p.

PRIMARY PRODUCTION

- European reserves:
  - Assumptions on gallium concentration
  - Assumption on extraction rate: 40%

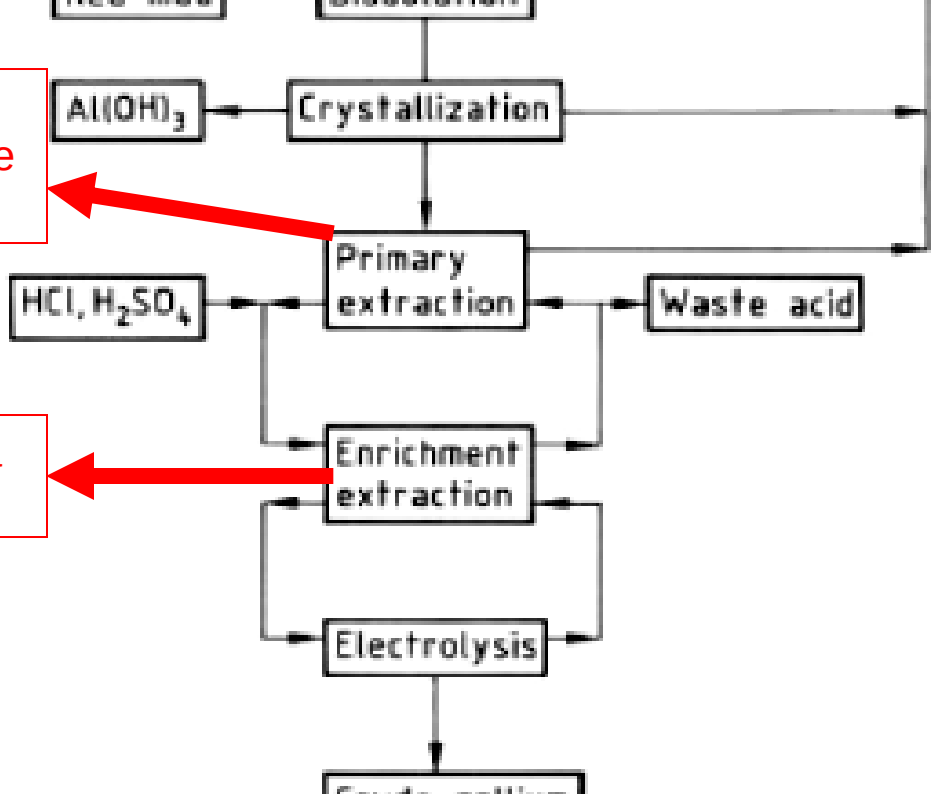


  - Effective extraction rate: < 2%

EUROPEAN COMMISSION JOINT RESEARCH CENTRE - Institute for Energy and Transport
(JRC) (2011), *Critical Metals in Strategic Energy Technologies : Assessing Rare Metals as Supply-Chain Bottlenecks in Low-Carbon Energy Technologies*, rédigé par MOSS R.L. *et al*, European Commission

PRIMARY PRODUCTION

- « Rhône-Poulenc » process for extraction



1) Liquid-liquid extraction with Kelex 100 in kerosene (with some Al, Na)

2) Separation from Al, Na using HCl

Al production (Bayer)

Ga extraction

CLASSEN M *et al* (2009), « 3. Gallium, semiconductor-grade, in *Life Cycle Inventories of Metals*, ecoinvent v2.1 report No. 10 (2009), pp. 13-22

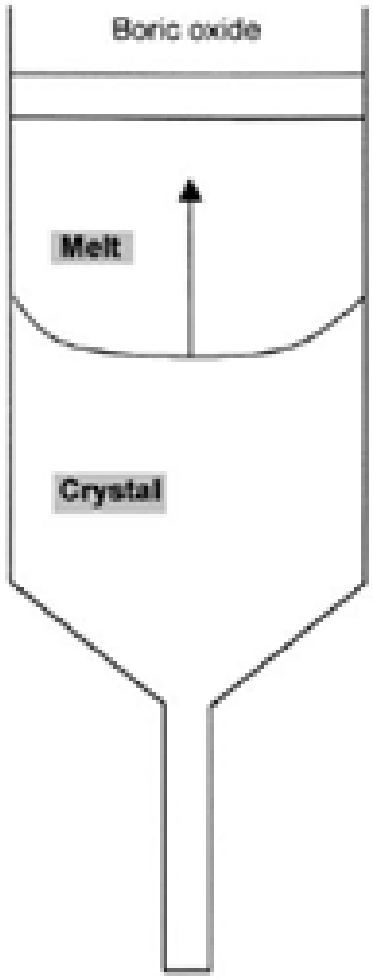
Primary production

- Need for refining
  - Obtained purity after extraction = max. 4N
  - Required for integrated circuits: 6-7N
- Refining options:
  - Vacuum distillation
  - Electrolytical refining

- Material processing for further application?

PRIMARY PRODUCTION

- For integrated circuits
  - Monocrystalline GaAs production for chips: Vertical Gradient Freeze (VGF)



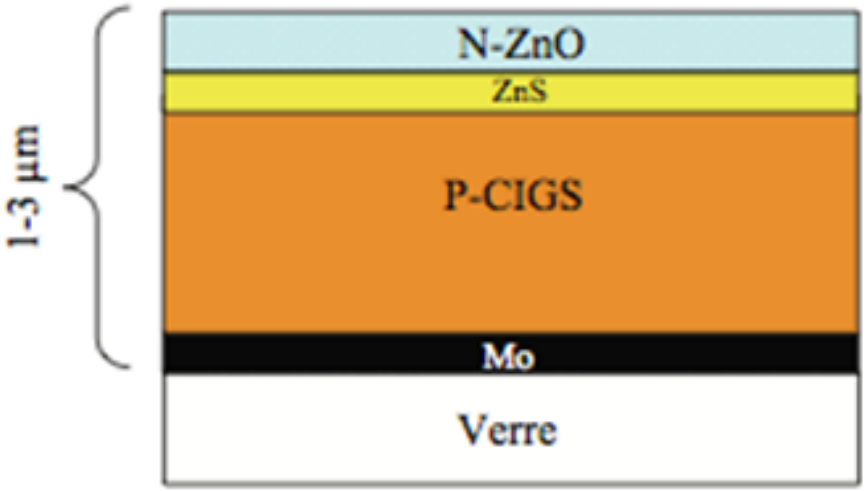
  - Followed by:
    - Slicing into wafers
    - Etching
    - Epitaxial growth of layers: HVPE,…
    - Cutting into chips

Ga losses:
-In boric oxide
-In cutting and grinding operations

GRANT I.R. (2001), « III–V Compound Semiconductors: Growth », in *Encyclopedia of Materials: Science and Technology*, pp. 1441–1453, Elsevier

PRIMARY PRODUCTION

- For photovoltaics: CIGS technology
  - « Thin film » or « second generation » PV
  - Sputtering (or CVD)



Primary production

- For LED and lasers: GaAs, GaN, GaP, GaSb
- Special alloys:
  - For Ga-In-Sn for thermometers
  - For magnets
  - For biomedical imaging, dental alloys,…

PRIMARY PRODUCTION

- Environmental impact of raw Ga:
  - Climatic impact ~ silver
  - 205,33 kg eq CO_2/kg (source: Ecoinvent – impact: IPCC 2007 – 100 years – 6N Ga)
- Environmental issue for PV panels:
  - CVD: most energy intensive step
  - Payback time: CIGS > Si
  - Expected improvements
- Health issue:
  - GaAs: cancer
  - AsH_3: lung, heart,… diseases

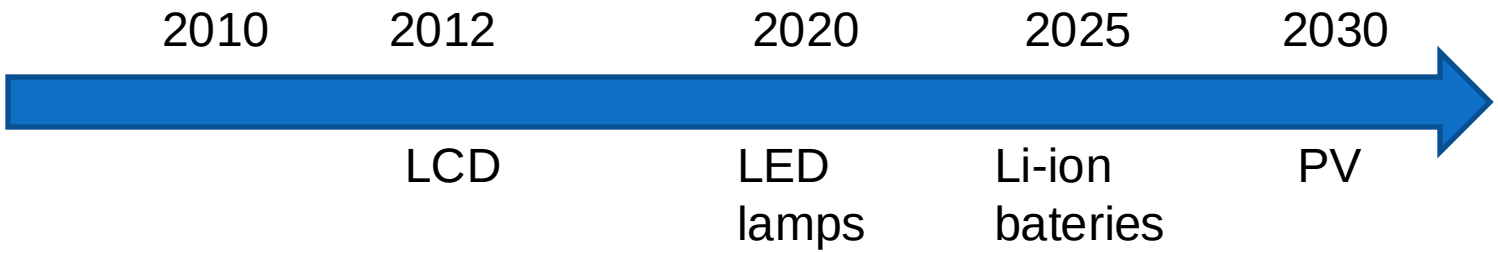
Recycling, to mitigate these impacts?

-Ecoinvent Centre (2010), ecoinvent data, v2.2. ecoinvent reports No.1-25, Swiss Centre for Life Cycle Inventories, Dübendorf, 2010, retrieved from: www.ecoinvent.org

-MOHR N. J. et al (2007), « Life Cycle Assessment of Thin-fim GaAs and GaInP/GaAs Solar modules », in *Progress in Photovoltaics : Research and Applications*, vol 15, pp. 163-179

SECONDARY PRODUCTION

- Sources of waste
  - Process scraps: 80% losses in MOCVD & MBE (source: IMEC) – 10-20 T
  - End of life products: « urban mine »

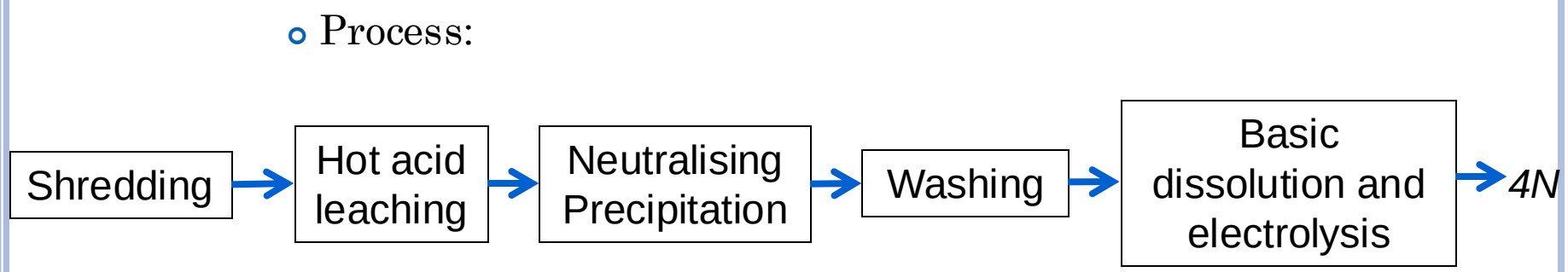


  - Recent demand met using stocks or secondary materials

AGENCE DE L'ENVIRONNEMENT ET DE LA MAÎTRISE DE L'ENERGIE (ADEME) (2010b), *Etude du Potentiel de Recyclage de Certains Métaux Rares : Partie 2*, rédigé par BIO Intelligence Service, ADEME, 153 p.

SECONDARY PRODUCTION

- Recycling from production scraps:
  - Little data
  - According to Neo Material: 140 tons (50% of total production)!
  - Semiconductors:
    - 90% of the scraps are recycled!
    - Process:



- Waste caracterisation: wafer production: Ga content

Broken wafers, out of dimensions parts,…	**39-48%**
Powder from cutting	30-46%
Polishing residues	< 1%

-US Geological Survey (USGS) (2003), *Recycling-Metals*, USGS, 16 p.
-FEDOROV V. A. *et al* (2006), « Preparation of High-Purity Gallium from Semiconductor Fabrication Waste», in *Inorganic Materials*, Vol. 42, pp. 570-589

SECONDARY PRODUCTION

- Recycling from production scraps: (2)
  - CIGS:
    - Not too critical: efficiency = 50%
    - Internal recycling at UMICORE Hoboken
    - Applied to the vacuum chamber dust
    - Product: concentrated gallium hydroxide

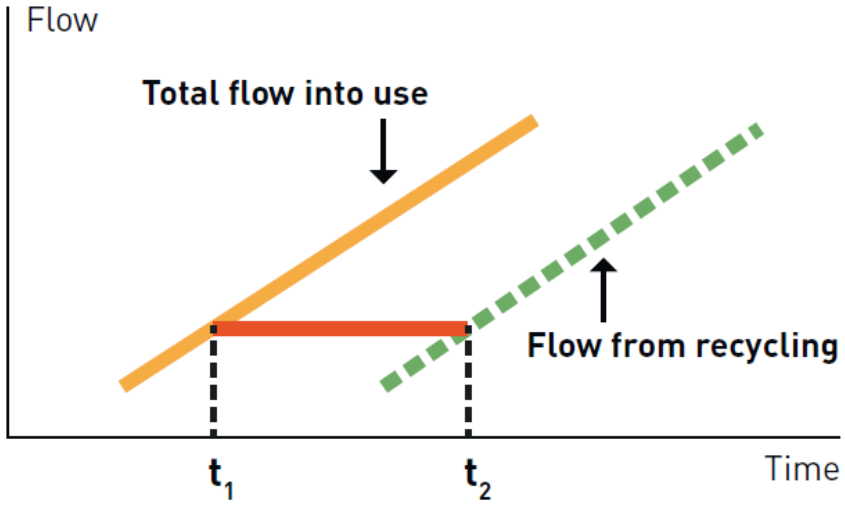
SECONDARY PRODUCTION

- Recycling from EoL products: does not exist!
  - Ga is very dispersed in LED, CIGS and circuits
  - Low price: 300 $/kg → economic return?
  - Future increase?
  - Carbon footprint of primary Ga is not high enough

- And more generally
  - Confidentiality
  - Price difficult to foresee
  - Crisis

Conclusions and perspectives

- Scarce data on scraps
- Collecting Ga containing EoL goods:
  - Control flows
- Recovery of Ga from EoL goods?
  - Composite materials: separation
  - Trace elements in materials
- Need for a LCA in order to assess the potential processes for secondary Ga processing
  - Energy bill
  - Mineral resources
  - Clean recycling?
- Time aspect



UNEP (2011), Recycling rates of Metals – A Status Report, 48p.

Conclusions and perspectives

- Accounting for:
  - Process losses
  - The absence of EoL recycling
  - The increasing demand
- Should we:
  - Develop recycling technologies?
  - Produce more primary Ga?
  - Reduce the consumption via ecodesign?
    - CVD processes
    - Consumers goods

Thank you for your attention!

4MAT

- 3 Professors
- 10 administrative and technical staffs
- ~ 20 researchers: PhDs, post-docs, researchers under industrial contracts (chemists, metallurgists, engineers in chemistry and material science, physicists)
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RESEARCH AXES

- 4MAT is interested in the full life cycle of materials (mostly inorganic) along four major research axes:
  - Synthesis and characterization of bulk and (thin) layered materials
  - Structure-Properties Relationships
  - Reactivity at interfaces including surface treatments
  - Recycling and valorization of secondary materials
  - The studies are developed from nano- to macro-scale. The research spans from purely fundamental studies to the design of pilot installations.

RESEARCH AXES

- Surface modifications and thin films deposition (including nanostructured samples) by plasmas (PVD, PECVD) and the relationship between the deposition conditions and the functional properties
- Innovative thermomechanical treatments : microstructure optimization, texture and phase transformations
- Mechanisms of defaults formation in small size materials
- Reactivity of hydraulic materials and incorporation of secondary materials
- Recovery of metals
- Life cycle analysis of materials