6. Germanium

Germanium is a hard and brittle semi-conducting metal discovered in 1886. Its position (IV A) in the periodic table (C-Si-Ge-Sn-Pb) indicates that it has properties similar to silicon. Germanium was initially used industrially in transistors due to its semi-conductor properties. It was later on replaced by silicon, which has better behaviour with respect to temperature. Its semi-conductor properties, however, remain of strong interest in some high-performance applications such as photovoltaics. It is now mostly used in fibre optics to increase their refractive index (reduce transmission losses) and in infrared detection/vision due to its transparency to infrared radiation. Furthermore it is used as a catalyst in organic chemistry.[1]

Recycled germanium is estimated by USGS to represent about 30% of the worldwide consumption. This consists of a notable (60%) fraction of germanium being discarded as scrap during the processing of most optical devices, which can then be recycled.[2] Recycling rates for fibre optic scrap are reported as high as 80%.[3] As a consequence, about 50% of the germanium metal used for electronic and optic are recycled in short cycle.

Germanium is not mined as a principal metal but is obtained as a by-product of zinc refining and from fly-ash of coal-fired power plants.[4] Currently, the production of germanium is dominated by China, followed by the Ukraine and Russia (see Figure 1). The price of germanium reached a very high level in 2011 (1450 US$/kg in 2011; zone refined germanium producer yearend price; see also Figure 2).[2]. After decreasing until the middle of 2012, the price of germanium rose back to an even higher level than before recently within one year (2013).[5]

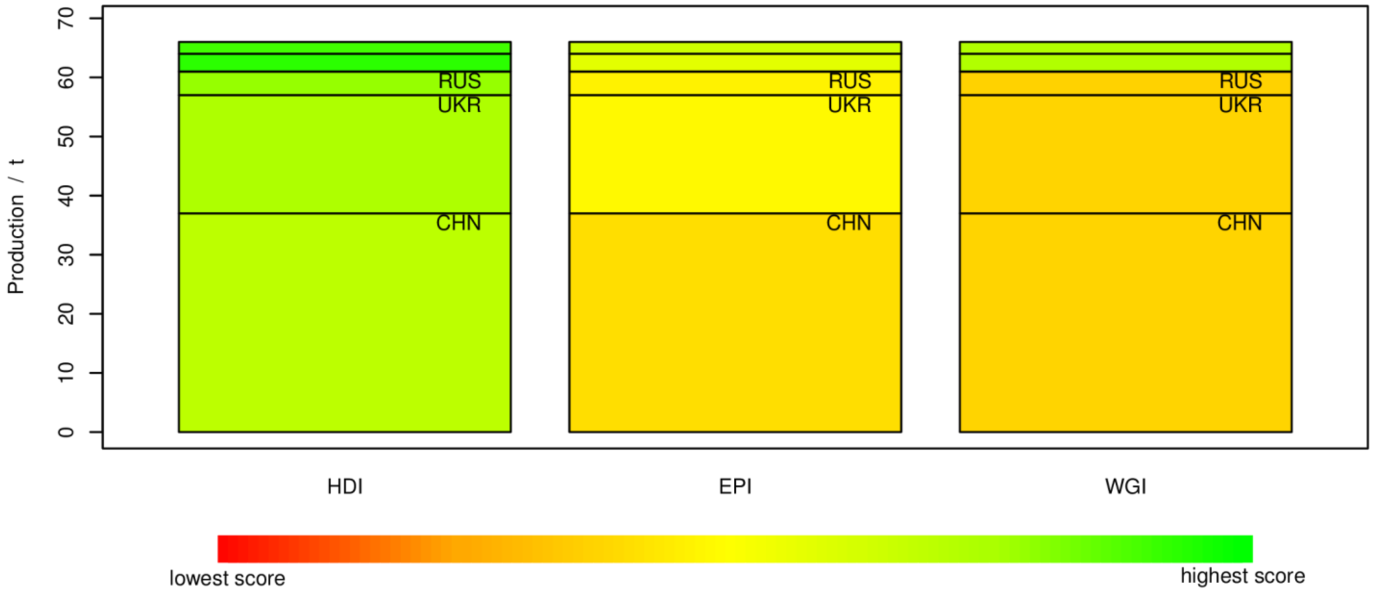

Figure 1: Distribution of germanium production[6] and corresponding scores of the producing countries in the Human Development Index (HDI),[7] Environmental Performance Index (EPI),[8] and World Governance Indicators (WGI).[9] Both the EPI and WGI are used to assess supply risks with the EU methodology for determining critical raw materials.[10] CHN = China; UKR = Ukraine; RUS = Russia.

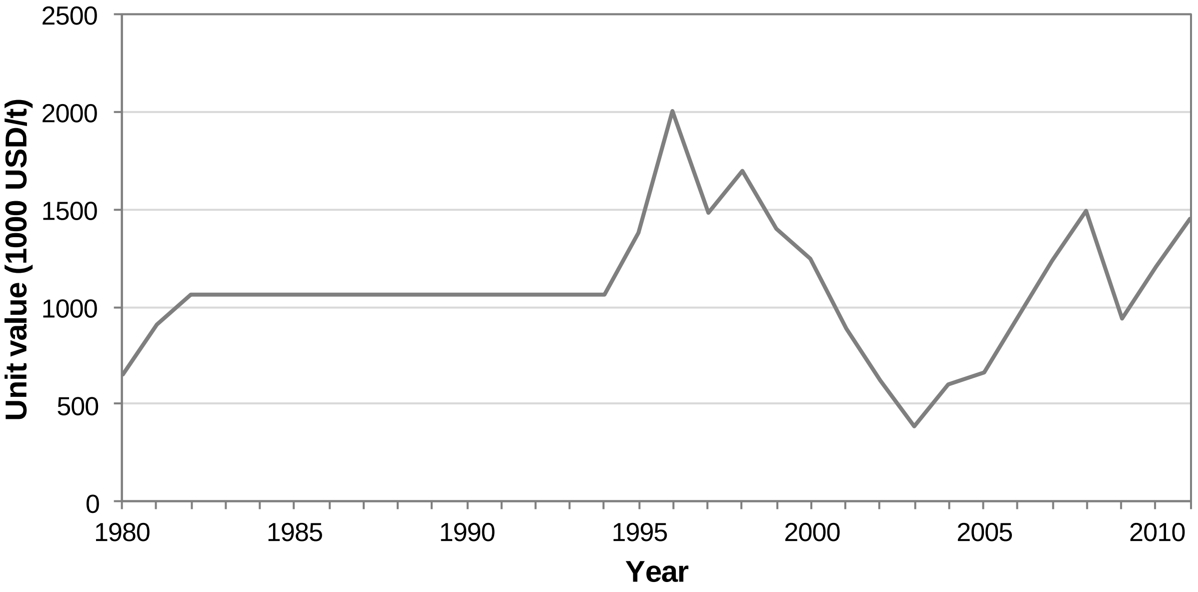

Figure 2: Germanium price development during 1980 – 2011. The unit value is the value of 1 metric ton (t) of germanium metal apparent consumption (estimated).[11]

Uses and substitutability

Germanium is used mainly in three forms[12]:

- Germanium metal: in the area of infrared optics, photovoltaics and other electronic applications (totalling about 45% of world demand);
- Germanium oxides (GeO_2): as catalyst for PET production (particularly in Japan), which accounts for 25% of world use;
- Germanium chlorite ($GeCl_4$): for fibre optic production (particularly in the USA), accounting for about 30% of global use.

Fibre Optics

This is considered the major use of germanium worldwide, accounting for 30-50% of use[12]. Germanium is used as a doping element in optical fibres, which contain approximately 4% germanium, the rest being silicon oxide. The function of germanium in optical fibre is to increase its refractive index, helping to contain the light within the fibre and enabling the transmission of the digital signal. This technology is a strong enabler of today's connectivity, forming the backbone of telecommunications and internet systems. Uptake will continue to increase in line with the current trend to digitally connect final consumers through fibre optics (Fibre to the Home – FTTH ; Fibre to the Building – FTTB).

As may be expected for such an important application, there is existing research to develop and improve fibre optic-based data transport which has spawned new fibre technologies: photonic hollow fibre (from Corning, the main fibre optics producer), fibres with tellurium layers, "OM2" fibres and erbium-doped fibres that enable optical signal amplification[12], some of which (e.g. hollow-fibre) are based on germanium-free technology.[13] Although germanium has been preferred for fibre optic doping, phosphorous-based doping

(P_2O_5) can also be used to raise the refractive index of silica, and other doping elements can be used to decrease this refractive index.[14,15]

Polymerization catalyst

Germanium dioxide (GeO_2) is a catalyst for the polymerisation of polyesters. Production of polyethylene terephthalate (PET), used for example in plastic bottles, is a major use.[2] Polymerization of resins to produce PET can also be achieved using alternative catalysts. Sb_2O_3 is a possible alternative and has been historically used for PET production, in particular in the US. Its potential health effects ("limited evidence of carcinogenic effects") is, however, a cause of concern although different organisations have reported that its use for PET production is safe under normal circumstances.[16] Further potential substitutes are antimony triacetate, an aluminium-based catalyst (identified by Toyobo) and a titanium-based catalyst (but which has the disadvantage of giving a yellowish colour to PET).[1,12]

Infrared optics

Germanium, being transparent to infrared radiation, is used to make lenses and window panes for infrared detectors and cameras, both in the military and the civilian sector. Both the lens and the detection sensor in which the infrared radiation is converted to electricity typically use germanium. It is thus used in numerous applications such as surveillance, night vision and satellite systems.[1]

Zinc selenide can substitute for germanium metal in selected infrared applications, but with lower performance.[2] Tellurium-based glass has also been announced as a potential substitute for infrared-based applications.

Parts for electrical and solar equipement

In the domain of photovoltaics (PV), germanium is used mostly in high-performance multi-junction cells (typically III-V cells). Due to high costs, these cells have been historically used in premium applications where high performance per surface and weight ratio was important, namely the PV panels used in satellite systems.

With the development of Concentrated Solar PV (CPV) on-ground systems, it becomes possible to use less PV cells by concentrating the solar rays on a smaller surface through and optical device (e.g. Fresnel lens), which reduces the pressure on cost. Multi-junction cells used in conjunction with on-ground CPV systems thus have a potential for future development. Germanium is typically used in the bottom-cell part of triple-junction PV, for the substrate, base and emitter layers, thanks to its lattice constant, robustness, low cost, abundance and ease of production. Germanium is very useful in capturing longer wavelengths. Current triple-junction cells having now reached efficiency levels close to their theoretical maximum (>43%). Research has developed towards even higher performance through the study of quadruple-layer multi-junction cells. In terms of substitution, it can be noted that triple-junction and quadruple-junction cells can also be based on non-germanium materials (e.g. containing InGaP, AlGaInP, InGaAsP, InGaAs materials).[17] This technology is, however, still at the research level.

On the electronic side, the specific SiGe transistors benefit from the low-cost of silicon processing and of the high-speed switching characteristics of germanium. Reduced energy consumption of SiGe transistors with respect to silicon-based transistor creates a strong potential for the third generation of mobile phones with high-speed wireless applications.[12] Germanium is also used in high-brightness LEDs.

Silicon can be a less-expensive substitute to germanium in some electronic applications.[2] The fact that such substitution is not yet in place relates to the higher performance achieved when using germanium. Some metallic compounds can be used for high-frequency electronics and some light-emitting diode applications.

Others

Other diverse uses of germanium exist, for example: use as an alloying element (0.35%) for tin, or Al-Mg alloys, to increase their hardness; soldering material (12% Ge / 88% Au) for gold-based dental prosthesis; luminescent material (red-coloured); photographic and wide-angle lenses; ceramics, with (Na_2O/TiO_2 or K_2O/Ta_2O_5; gamma-ray detector $Bi_2(GeO_3)_3$; bismuth germanate oxide crystals (BGO – $Bi_4Ge_3O_{12}$) for various detection technology (scintillation, tomography, gamma spectroscopy); fluorescent paint ($MgGeO_3$); superconductors (Nb_3Ge); thermocouple and thermoelectricity; medication (diverse uses currently under investigation); germanium-containing products are sold in the US as antioxidants.

Summary

Germanium material has demonstrated to be well suited for several major applications with comparable importance (~25-30% of Ge usage): fiber optics, infrared optics and polymer catalysts.

Due to a history of using a germanium-free catalyst for PET production in the USA, the substitution by Sb_2O_3 is judged reasonable but suffers from persisting concerns about possible health effects.

Both for fiber-optics and infrared optics, no evidence has been identified of cheap and off-the-shelf substitution solutions for the breadth of these applications. Possibilities exist, but are overall either characterized by a likely loss of performance, a lack of industrial maturity (e.g. still at the research level), or an uncertainties about their ability to fulfil all the requirements of the product/solution or industrialization capabilities. In the case of fiber-optics, which has nowadays almost a status of a commodity-product, the production volume puts a specific pressure on the substitution potential. For infrared-optics, although the use is less wide-spread, the market has been evolving towards wider use (e.g. security, maybe tomorrow consumer equipment).

For solar applications (photovoltaic, e.g. satellite PV panels) and high-profile electronic applications, it is judged that the level of requirements justifies the consideration as “premium” applications, where performance largely dominates cost issues.

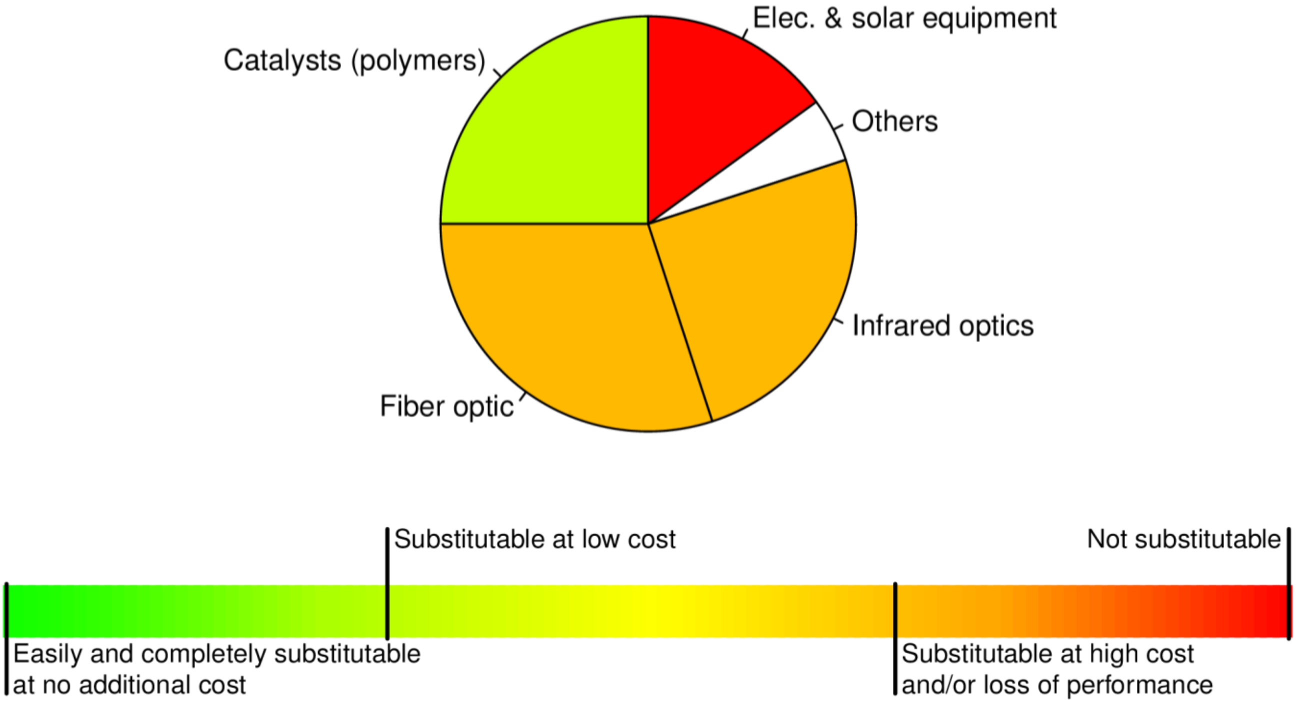

Figure 3: Distribution of end-uses[10] and corresponding substitutability assessment for germanium. The manner and scaling of the assessment is compatible with the work of the Ad-hoc Working Group on Defining Critical Raw Materials (2010).

References

1 Butterman W.C., Jorgenson JD (2005) Germanium. Open-File Report 2004-1218

2 Guberman, D. E. (2013) Germanium, in: U.S. Geological Survey (ed.) Mineral commodity summaries 2013

3 Bell Labs - Lucent Technology Bell Labs Innovative Germanium-Recovery Process is Economically, Environmentally Friendly. Science Daily. http://www.sciencedaily.com/releases/1997/10/971023172421.htm. Accessed 23 August 2013

4 Willis P, Chapman A, Fryer A (2012) Study on by-products of copper, lead, zinc and nickel

5 Metal Bulletin Germanium Metal Rotterdam $/kg: Latest Metal Prices Tracking and Comparison Tool. http://www.metalbulletin.com/My-price-book.html?price=42087. Accessed 3 September 2013

6 Reichl C, Schatz M, Zsak G (2013) World Mining Data: Production of Mineral Raw Materials of individual Countries, by Minerals. in 2011 in metric tonnes

7 United Nations Development Programme (UNDP) (2013) The 2013 Human Development Report – "The Rise of the South: Human Progress in a Diverse World"

8 Yale Center for Environmental Law and Policy (YCELP) (2013) Downloads | Environmental Performance Index. http://epi.yale.edu/downloads. Accessed 26 July 2013

9 World Bank Group (2013) Worldwide Governance Indicators. http://info.worldbank.org/governance/wgi/sc_country.asp. Accessed 26 July 2013

10 Ad-hoc Working Group on defining critical raw materials (2010) Critical raw materials for the EU: European Commission

11 Kelly, T., George, M., Jasinski, S., Gabby, P., Guberman, D. (2012) Germanium: Supply-Demand Statistics, in: U.S. Geological Survey Minerals Information

12 Christmann P, Angel JBL, Barthelemy F, Benhamou G, Billa M, Gentilhomme P, Hocquard C, Maldan F, Martel-Jantin B, Monthel J (2011) Panorama du marche 2011 de germanium Rapport Final. BRGM/RP-60584-FR

13 Amezcua Correa R (2009) Development of hollow-core photonic bandgap fibre free of surface modes. Ph.D. thesis. Southampton

14 Brown, T. G. (1995) Optical Fibers and Fiber-Optic Communications, in: Bass M (ed.) Handbook of optics, 2nd edn., pp. 10.1-10.50. New York: McGraw-Hill

15 CEA internal. Personal communications

16 International Antimony Association (2012) Antimony trioxide. http://www.antimony.com/files/cms1/publications/i2a-factsheet-trioxyde-v3.pdf. Accessed 30 August 2013

17 Luque A, Hegedus S (2011) Handbook of photovoltaic science and engineering, 2nd edn. Chichester: Wiley