8. Indium

Indium is a silvery-white metal that is chemically and physically similar to gallium and tallium (all in Group III of the periodic table). With a melting point of 157 °C, indium belongs to a group of low melting point post-transition metals that are very soft and malleable. A particular concern for indium criticality is its main use in growing and emerging markets. Indium is exclusively used in electronics applications that have grown and are forecasted to continue to grow at high rates of 5 – 30% per year[1–3]. A prime example is the use of indium doped tin oxide (ITO) in flat panel displays (LCD, plasma screens, e-paper), which constitute the major use (75%) of indium [4]. The demand for flat panel displays quickly accelerated due to increasing use of flat screen televisions, PC monitors, notebooks and tablets and mobile phones. At the same time organic electronics, such as active-matrix organic light-emitting diode (AMOLED) displays, organic light-emitting diode (OLED) lighting and photovoltaics, also using ITO, and thin film $CuInGaSe_2$ (CIGS) photovoltaics are emerging technologies forecasted to also grow quickly in the coming decade[1,3,5]. However, there is a significant awareness of the indium criticality in the electronics industry and considerable academic and industrial effort is put into the development of substitutes for indium[6]. The price of indium represents this fact in one dimension as well, since the price was already high and even increased to an annual average value of 720 US$/kg in 2011[*].[4] The price decreased in the year 2011 and then was stable above 500US$ per kg in 2012. In 2013 the price started to increase again.[7]

Indium is mainly obtained as a by-product from zinc concentrates. While China is the largest producer worldwide, there is also significant production in Canada, Korea and Japan.

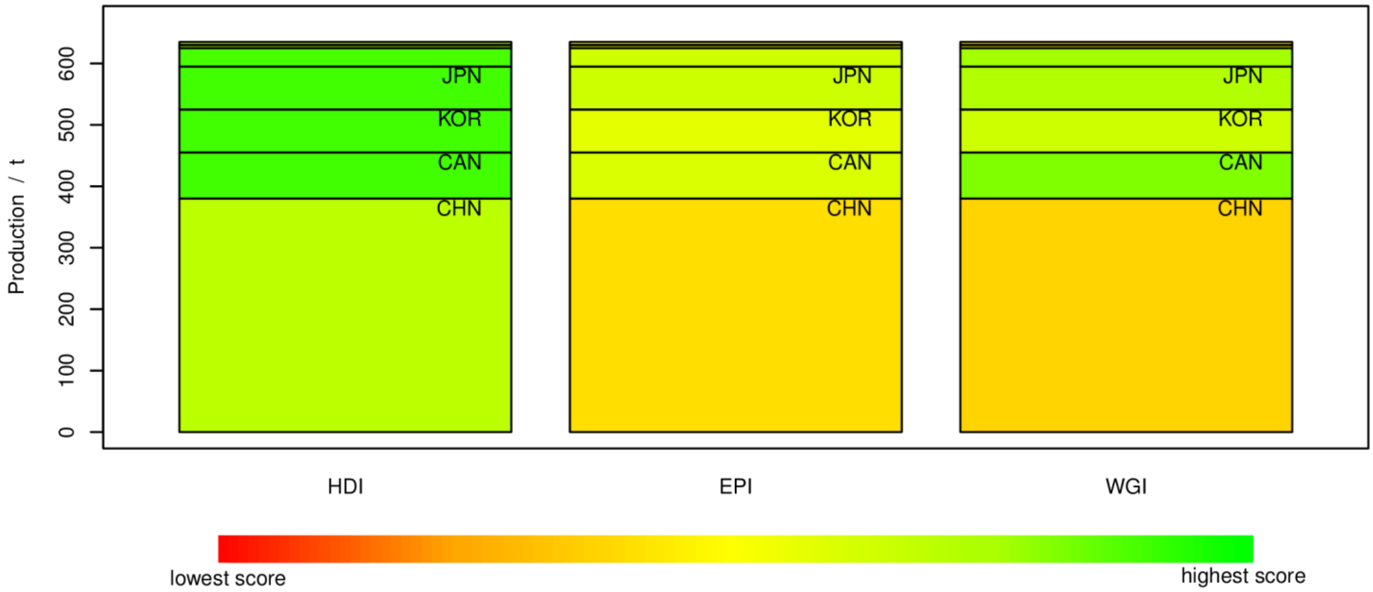

Figure 1: Distribution of indium production[8] and corresponding scores of the producing countries in the Human Development Index (HDI)[9], Environmental Performance Index (EPI)[10], and World Governance Indicators (WGI)[11]. Both the EPI and WGI are used to assess supply risks with the EU methodology for determining critical raw materials [12]. CHN = China; CAN = Canada; KOR = South Korea; JPN = Japan.

[*] New York dealer: Price is based on 99.99%-minimum-purity indium at warehouse (Rotterdam); cost, insurance, and freight (in minimum lots of 50 kilograms).

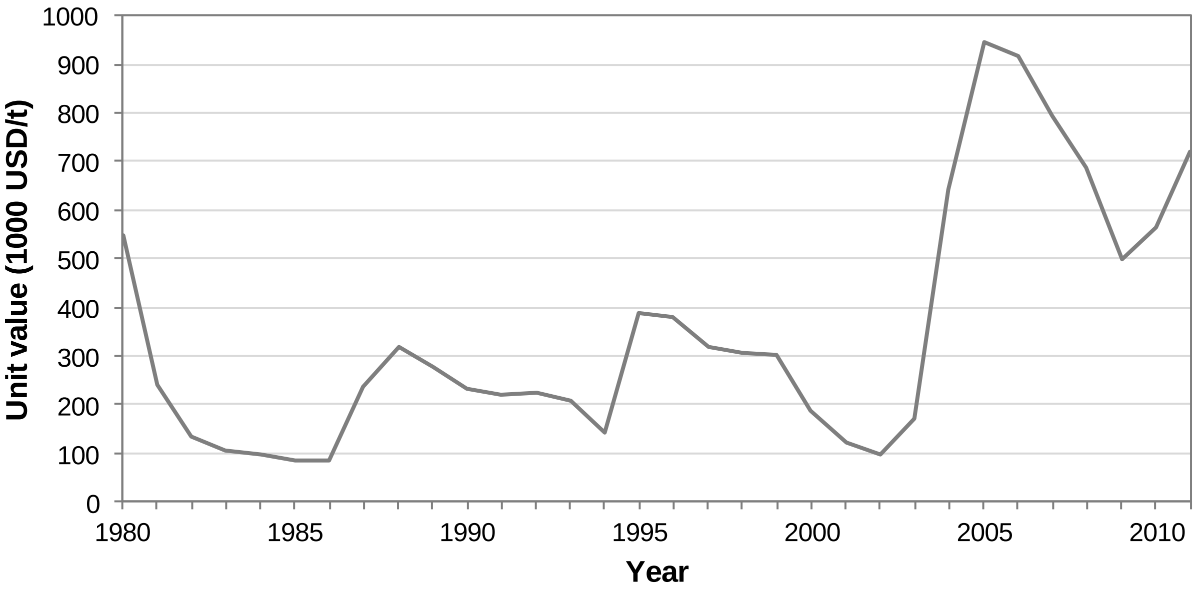

Figure 2: Indium price development during 1980 – 2011. The unit value is the value, in current dollars, of 1 metric ton (t) of indium apparent consumption (estimated).[13]

Uses and substitutability

The uses of indium can be grouped into three types of indium compounds[14]:

- **Indium-tin-oxide (ITO) thin films for**
  - Flat panel displays
  - Optoelectronic windows (architectural glass / windscreens)
- **Indium compounds (III-V semiconductors) for**
  - LEDs
  - Integrated circuits
  - Thin film $CuInGaSe_2$ (CIGS) solar cells
- **Alloys for**
  - Low-melting point solders
  - Dental alloys
  - Surface coatings
  - Minor alloys

Flat panel displays

The major use of indium is found in thin film indium-tin-oxide (ITO) windows for flat panel displays[2,4]. Television screens, PC monitors, notebook screens and touchscreens on mobile phones and tablets all require a window that is electrical conducting and optically transparent[15]. The electrical conductivity facilitates the voltage-triggered switching of the pixels in a display. ITO is a transparent conductive oxide (TCO) that combines a good conductivity with a high optical transparency. In addition ITO has a high atmospheric stability, i.e. durability, and allows accurate etching of the electrode arrays used to address individual pixels. ITO consists of 90% In_2O_3 and 10% SnO_2 corresponding to a 75 wt% indium content. It is supplied to the flat panel display manufacturing industry as ITO targets for sputter tools. In manufacturing the in-line sputter tools deposit thin (100 nm) ITO films at high rates on large area display glass panels.

The flat panel display industry is aware of the criticality and the associated price fluctuations of indium. Considerable R&D effort has been and continues to be focused on finding alternatives for ITO[6]. Other TCOs, in particular aluminium doped zinc oxide (AZO) and fluorine doped tin oxide (FTO) are possible substitutes for ITO. Both are produced on an industrial scale and at lower cost than ITO. However, in performance both AZO and FTO lags behind ITO. The specific conductivity is respectively a factor of 2 and 4 lower requiring thicker films for a similar electrical performance, which reduces the transparency of the screen. Also AZO and FTO cannot be etched as accurately as ITO, preventing their use in high resolution displays, like the latest generation of mobile phone touchscreens. Finally, AZO is sensitive to degradation by moisture. Emerging amorphous TCOs, like gallium-indium-zinc-oxide (IGZO / IZGO), indium-zinc-oxide (IZO) and zinc-tin-oxide promise properties equal or better than ITO, but are estimated to take at least 5 years to commercialisation. Moreover, although the concentration is lower IGZO and IZO still contain indium.

Next to the TCOs there is a range of transparent conductive film technologies under development with an estimated time-to-market of 5 – 10 years, in particular:

- Ultrathin metal films and zinc oxide-metal-zinc oxide multilayers
- Carbon nanotubes and metal nanowire films
- Graphene films
- Organic transparent conductors (PEDOT:PSS)
- Printed metal grids

All these alternatives under perform on at least one of the properties required for flat panel display application. Apart from the multilayers and the metal grids that outperform ITO, these alternatives do not (yet) exhibit the same good electrical conductivity at a high optical transparency as ITO. The ability to etch the films and the durability of the films needs to be established. The viability of manufacturing on industrial scale at competitive costs still has to be proven for all these technologies.

Research and development into display technologies that do not require ITO started form the emerging field of flexible electronics, like organic LED (OLED) displays on foil. Here the low mechanical stability of ITO, which restricts display flexibility, presents an additional driver for finding alternatives to ITO. An organic transparent conductive PEDOT:PSS with a printed silver grid is able to substitute ITO in prototype flexible OLED displays. However, their limited durability has prevented commercialization of ITO-free flexible displays up to now. Active-matrix OLED displays on glass have been introduced in the mobile phones market recently, but these rigid displays use ITO. The only alternative ITO-free display technology available today is LED displays, as used in LED television screens, signage and billboards. LED displays do not need transparent electrodes because individual LED pixels are addressed form the display backs-side. However, indium-gallium-nitride-based diodes are the main active components in LED displays.

In conclusion, substitution of flat panel displays containing ITO, either by an ITO alternative or a different display technology, is currently not possible without a loss of performance or the use of another indium containing component.

Optoelectronic windows

In addition to flat panel displays, another range of applications uses ITO on glass to obtain specific optoelectronic functionalities. The combination of electrical conductivity with a high optical transparency of ITO is used to add an electrical function to glass with a minimum loss in transparency. Also in optoelectronic applications indium is procured as ITO targets for thin film ITO film sputtering.

The main optoelectronic window application is architectural glass[15]. Low-emissivity coatings containing ITO reduce heat losses through windows. In these coatings ITO is part of a multilayer stack including transparent silver films and various atmospheric barriers and adhesion layers. An emerging application in architecture is smart windows that allow light balancing, temperature regulation by IR reflection and integration of transparent sensors. Light balancing is, for example, achieved by controlling the light transmission through an electrochromic film containing ITO. Similar ITO coated smart windows are gradually entering the automotive market. Currently, some cars are equipped with defogging windscreens and defrosting headlights through heating of a resistive ITO coating.

Fluorine-doped tin oxide (FTO) is a substitute for ITO in architectural glass. FTO is applied in-line immediately after glass production in float glass lines. The lower specific conductivity of FTO compared to ITO is not an issue because a low conductivity is required for low-emissivity coatings[15]. Also FTO has a similar high resistance to atmospheric degradation as ITO. In well-packaged low-emissivity multilayers, such as inside double glazing, zinc oxide and aluminium-doped zinc oxide (AZO) are also a feasible substitutes for ITO. The packaging protects the zinc oxide against degradation by moisture from the atmosphere. Heated windscreens and headlights require higher conductivities making FTO and AZO less suitable substitutes. Additionally, the sensitivity of AZO to atmospheric degradation excludes its use in these applications. Emerging amorphous TCOs, like gallium-indium-zinc-oxide (GIZO / IZGO), indium-zinc-oxide (IZO) and zinc-tin-oxide promise properties equal or better than ITO, but are estimated to take at least 5 years to commercialisation. Moreover, GIZO and IZO still contain indium, although the concentration is lower.

A growing application of optoelectronic windows is thin film solar cells. Highly conductive and transparent windows are needed to let sunlight enter the solar cells and transport the generated current away. ITO has been used a window layer in the so-called second generation solar cells, based on thin film cadmium telluride (CdTe), amorphous silicon (aSi) and copper-indium-gallium-diselenide (CIGS). However, FTO or AZO are now state-of-the-art in industrial manufacturing of these thin film solar cells. For the third generation solar cells, organic solar cells (OPV) and dye-sensitized solar cells (DSSC) that are forecasted to be commercialized in 5 to 10 years, ITO is the preferred window material. The chemical aggressiveness of the electrolyte used in DSSC makes replacement of ITO impossible for now. Just as for the flat panel OLED displays, organic transparent conductive PEDOT:PSS with a printed silver grid are able to substitute ITO in OPV, in particular for flexible modules.

In conclusion, substitution of ITO in optoelectronic windows is currently possible for architectural windows, but this is not possible without a loss of performance for heated windscreens and car lights. For current thin film solar cells technologies ITO alternatives are already in place and for next generation solar cells ITO substitution will be possible.

Low melting point alloys

Indium has one of the lowest melting points of all metals and forms low melting point (i.e. room temperature to 156 °C) alloys with tin, silver, lead and ternary or quaternary combinations thereof. Indium alloys are therefore used in the electronics industry for soldering on temperature sensitive materials in moulded interconnect devices, flexible printed circuit boards or of temperature sensitive components in photonic applications, e.g. bonding of LEDs. Indium-lead is used for soldering on gold bond pads on printed circuit boards (PCBs) because of the better durability compared to tin-based alloys. Indium alloys are also highly ductile even at very low temperatures and are used to bond materials, (such as, quartz, glass and ceramics) with a large thermal expansion mismatch and in sealing of cryogenic equipment (e.g. liquefied gas production). Finally, indium is used to reduce mercury leakage in dental filling amalgams. Little effort has been put into finding alternatives for indium alloys, because they are used in relatively niche applications.

There is range of tin-based alloys with zinc and bismuth used extensively for soldering and bonding in the electronics industry. However, tin-alloys have melting points down to 150 °C, which is the maximum in the melting point range of indium alloys. Lead-based alloys enable lower melting point, but these have recently been banned by the EU in the RoHS (Restriction of Hazardous Substances) directive. Hence, only for the least thermally sensitive applications are tin-based alloys good substitutes for indium alloys. Tin-alloys can also be used for bonding on gold, but indium alloys were specially developed as an alternative to the tin-alloys. The so-called gold scavenging by bonding alloys resulting in destruction and failure of gold bond pads is much lower for indium alloys than for tin alloys. Substitution of indium alloys in cryogenic sealings by tin-based alloys is not possible, because tin alloys lose their ductility at low temperature.

Alternative bonding/soldering technologies to metal alloys have been developed as part of the search for lead-free solders in the last decade. Silver-filled conductive adhesives have found limited industrial use, because of the high costs associated with the silver-filling. Nanoparticle pastes, using the melting point reduction of materials on the nano-scale are an emerging alternative bonding technology, but still have a time-to-market of at least 5 – 10 years. In general, market introduction of alternative bonding technologies is hindered by the huge installed base of soldering equipment and the strong focus on low-cost and high reliability manufacturing in the electronics industry.

Indium-free dental fillings are widely used. Indium was specially introduced in dental filling amalgams to increase strength and reduce mercury leakage. Gallium based amalgams have also been developed, but are not preferred due to the criticality of gallium. Composite resin dental fillings are a general alternative to amalgam dental fillings. Although the durability of the composite fillings is marginally less, costs are slightly higher and application less easy composite dental fillings are a suitable alternative[16].

In conclusion substitution of indium alloys is currently possible in dental alloys, is possible for a number of low temperature bonding and soldering applications, but is not possible for cryogenic sealing.

In-compounds

Indium-containing semiconductors are currently a minor use of indium. Semiconductor compounds of indium, specifically InP are used in high-power and high-frequency electronics, for example high tech mobile phones and wireless applications. Optoelectronics devices such as laser diodes, photodiodes and LEDs use InP, InGaAs and GaInN because of their high electron velocity compared to silicon and their direct bandgap. The In-based semiconductors are part of the multilayer stacks used as the active component in LEDs and laser diodes. GaAs and SiGe are alternatives to InP exhibiting similar properties required for the high high-power and high-frequency electronics. However, both use other critical raw materials such as Ge and Ga. Zinc oxide (ZnO) has been investigated as an alternative semiconductor material in LEDs. However, the required p-type ZnO has limited stability making in not (yet) a feasible substitute. OLEDs are an emerging alternative lighting technology, but still lack the long-term stability to compete with solid state LEDs.

Copper-indium-gallium-diselenide (CIGS) thin film solar cells are a growing application that is forecasted to attain a significant share (20%) of the fast growing photovoltaic market in the coming decades. CIGS is an III-IV-VI semiconductor with a band-gap ideal for conversion of sun light into electricity and, as a thin film solar technology, it holds the potential of lower manufacturing costs and better product integration compared to the state-of-the-art silicon wafer based solar modules. CIGS solar modules are manufactured on an industrial scale by around five companies world-wide. The industrial and academic CIGS community is aware of the criticality of indium, but opinions on the need for substitution vary. A one-to-one material substitution by copper-zinc-tin-selenide/sulphide (CZTS) has become a significant R&D theme in the recent years[17]. However, with a record efficiency (2013 figures) of only 11.1% compared to 20.4% for CIGS solar cells, commercial production of CZTS modules is not expected within the coming 10 years. Also due to the strong cost reduction in the last 3 years, silicon based solar modules are an obvious substitute for CIGS apart from its limitation of integration in electronic devices and the build environment.

In conclusion, substitution of indium is at present mostly possible in semiconductor applications (high-power and high-frequency electronics applications and thin film solar cells) with the exceptions of optoelectronic devices (LEDs and laser diodes).

Summary

Indium cannot be substituted in its main field of application, flat panel displays, without a loss of performance or the use of another indium containing component, but substitution is possible in most other applications albeit sometimes at higher costs.

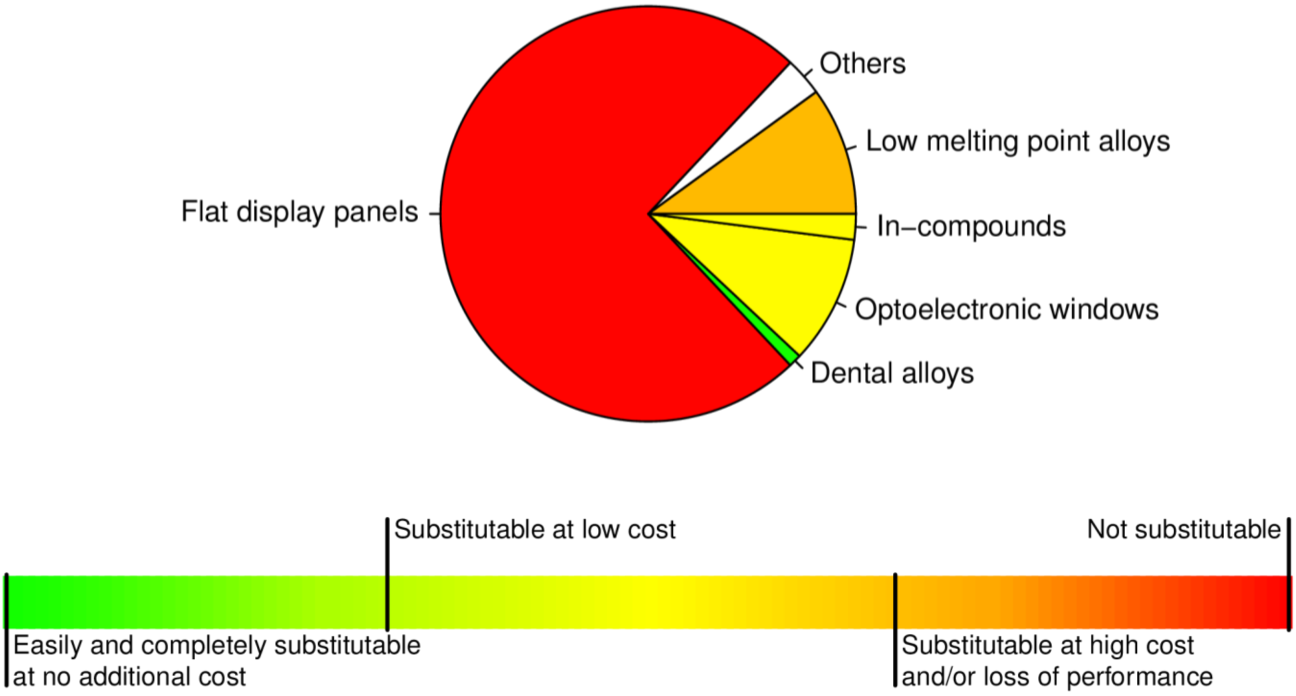

Figure 3: Distribution of end-uses and corresponding substitutability assessment for indium. The manner and scaling of the assessment is compatible with the work of the Ad-hoc Working Group on Defining Critical Raw Materials (2010).

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