Reduction and replacement of critical raw material used for transparent electrodes in flat screens, transparent electronics and solar cells

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Report lists 14 critical mineral raw materials

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Production 2006 (t)</th>
<th>Demand from emerging technologies 2006 (t)</th>
<th>Demand from emerging technologies 2030 (t)</th>
<th>Indicator 1) 2006</th>
<th>Indicator 1) 2030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
<td>152.6</td>
<td>28</td>
<td>603</td>
<td>0.18</td>
<td>3.97</td>
</tr>
<tr>
<td>Indium</td>
<td>581</td>
<td>234</td>
<td>1.911</td>
<td>0.40</td>
<td>3.29</td>
</tr>
<tr>
<td>Germanium</td>
<td>100</td>
<td>28</td>
<td>220</td>
<td>0.28</td>
<td>2.20</td>
</tr>
<tr>
<td>Neodymium (rare earth)</td>
<td>16,800</td>
<td>4,000</td>
<td>27,900</td>
<td>0.23</td>
<td>1.66</td>
</tr>
<tr>
<td>Platinum (PGM)</td>
<td>255</td>
<td>very small</td>
<td>345</td>
<td>0</td>
<td>1.35</td>
</tr>
<tr>
<td>Tantalum</td>
<td>1,384</td>
<td>551</td>
<td>1,410</td>
<td>0.40</td>
<td>1.02</td>
</tr>
<tr>
<td>Silver</td>
<td>19,051</td>
<td>5,342</td>
<td>15,823</td>
<td>0.28</td>
<td>0.83</td>
</tr>
<tr>
<td>Cobalt</td>
<td>62,279</td>
<td>12,820</td>
<td>26,860</td>
<td>0.21</td>
<td>0.43</td>
</tr>
<tr>
<td>Palladium (PGM)</td>
<td>267</td>
<td>23</td>
<td>77</td>
<td>0.09</td>
<td>0.29</td>
</tr>
<tr>
<td>Titanium</td>
<td>7,211,000.2</td>
<td>15,397</td>
<td>58,148</td>
<td>0.08</td>
<td>0.29</td>
</tr>
<tr>
<td>Copper</td>
<td>15,093,000</td>
<td>1,410,000</td>
<td>3,696,070</td>
<td>0.09</td>
<td>0.24</td>
</tr>
</tbody>
</table>

1. The indicator measures the share of the demand resulting from driving emerging technologies in total today's demand of each raw material in 2006 and 2030; 2) Ore concentrate
Indium Tin Oxide (ITO) thin films

Worldwide applications of virgin indium, 2010

Source: Indium Corporation (2011), The indium Market
https://setis.ec.europa.eu/mis/material/indium
Transparent electrodes on plastic substrates

<table>
<thead>
<tr>
<th>Inorganic materials</th>
<th>( \text{In}_2\text{O}_3 )</th>
<th>( \text{SnO}_2 )</th>
<th>( \text{ZnO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doping elements</td>
<td>( \text{Sn}, \text{F}, \text{Te} )</td>
<td>( \text{Sb}, \text{F}, \text{P} )</td>
<td>( \text{Al, In, Ga} )</td>
</tr>
<tr>
<td>Work function (eV)</td>
<td>4.1-5.5</td>
<td>4.2-4.4</td>
<td>4.3-4.4</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>3.5-3.7</td>
<td>4.0-4.5</td>
<td>3.2-3.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic material</th>
<th>PEDOT:PSS</th>
<th>PANI</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td><img src="image" alt="PEDOT:PSS" /></td>
<td><img src="image" alt="PANI" /></td>
<td><img src="image" alt="Graphene" /></td>
</tr>
<tr>
<td>Work function (eV)</td>
<td>5.1</td>
<td>4.5-4.7</td>
<td>4.5-5</td>
</tr>
</tbody>
</table>
Organic solar cells – on plastic

A complete process for production of flexible large area polymer solar cells entirely using screen printing- First public demonstration

Frederik Krebs and coll.

Physicist Alan J. Heeger
Nobel prize for chemistry in 2000

OPV INFINITY - 2014

http://www.nanotechwire.com
Transparent electrodes on plastic: oxide/metal/oxide

Organic solar cells

<table>
<thead>
<tr>
<th>Layer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Metallic electrode</td>
</tr>
<tr>
<td>LiF</td>
<td>Active layers</td>
</tr>
<tr>
<td>P3HT : PCBM</td>
<td>Transparent electrode</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Glass/Plastic</td>
</tr>
<tr>
<td>ITO</td>
<td>Metallic electrode</td>
</tr>
<tr>
<td>LiF</td>
<td>New electrodes</td>
</tr>
<tr>
<td>PET or glass substrate</td>
<td></td>
</tr>
</tbody>
</table>

New organic materials improve materials stability

New electrodes

oxide thin film (20 nm)
metallic thin film (7 nm)
oxide thin film (20 nm)
PET or glass substrate
Transparent electrodes on plastic: oxide/metal/oxide

Less quantity of material, higher mechanical resistance, very good electrical stability, figure of merit comparable to classical TCO

IMI – electrodes on plastic (2012)

- oxide thin film (20 nm)
- metallic thin film (7 nm)
- oxide thin film (20 nm)
- PET or glass substrate

Universal Exhibition Milan (2015)

Belectric-OPVIUS
<table>
<thead>
<tr>
<th>Layer</th>
<th>Target composition</th>
<th>Atmosphere conditions</th>
<th>Target-Substrate distance (cm)</th>
<th>Deposition current (mA)</th>
<th>Pressure ($10^{-2}$ mbar)</th>
<th>Depositio ntime (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>In 90 %, Sn 10%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>30</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>Au</td>
<td>Au 100%</td>
<td>Argon atm.</td>
<td>7</td>
<td>30</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>ITO</td>
<td>In 90 %, Sn 10%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>30</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn 98 %, Al 2%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>100</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>Au</td>
<td>Au 100%</td>
<td>Argon atm.</td>
<td>7</td>
<td>100</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn 98 %, Al 2%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>100</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Ti 100%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>100</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>Au</td>
<td>Au 100%</td>
<td>Argon atm.</td>
<td>7</td>
<td>100</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Ti 100%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>100</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>Bi 100%</td>
<td>Reactive atm.</td>
<td>7</td>
<td>30</td>
<td>2</td>
<td>160</td>
</tr>
<tr>
<td>Au</td>
<td>Au 100%</td>
<td>Argon atm.</td>
<td>7</td>
<td>30</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>Bi 100%</td>
<td>Reactive atm.</td>
<td>100</td>
<td>30</td>
<td>2</td>
<td>160</td>
</tr>
</tbody>
</table>
Ellipsometry - modelling

In ellipsometry, the variation of the amplitude and the phase difference between the perpendicular (p) and the parallel (s) components of the reflected light polarized, with respect to the plane of incidence, are measured. In general, reflection causes a change in the relative phase of p and s waves and in the ratio of their amplitudes.

\[
\tan \psi \exp(i\Delta) = \frac{R_p}{R_s} \quad (1)
\]

Where, \(R_p/R_s\) is the complex ratio of the Fresnel reflection coefficients. \(\psi\)—measure the amplitude ratio and \(\Delta\)—measure the relative phase change.

The measured ellipsometric spectra are fitted by minimizing the squared difference \(\chi^2\) between the measured and calculated values of the ellipsometric parameters \(I_s\) and \(I_c\). \(I_s\) and \(I_c\) are given by:

\[
I_s = \sin 2\psi \sin \Delta \\
I_c = \sin 2\psi \cos \Delta
\]

\[
\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 = \tilde{n}^2 = (n + ik)^2 = \sin(\theta)^2 \left[ 1 + \tan(\theta)^2 \left( \frac{1 - \tan(\psi) e^{i\Delta}}{1 + \tan(\psi) e^{i\Delta}} \right) \right]^2 \quad (3)
\]
Spectroscopic ellipsometry - linearly polarized incident light (right) changes to elliptically polarized light (left) after oblique reflection off of the sample. Modeling the change in polarization provides thin-film parameters such as thickness and optical constants.
## Ellipsometry - modelling

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>Ellipsometry</td>
<td>Profilometry</td>
</tr>
<tr>
<td>Refractive index</td>
<td>Ellipsometry</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>Optical transparency</td>
<td>Ellipsometry</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>Optical band gap</td>
<td>Ellipsometry</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>Ellipsometry</td>
<td>Electrical measurements</td>
</tr>
</tbody>
</table>
Figure 2. SEM micrograph of oxide single layer (bottom layer) and oxide/metal/oxide samples bottom and top layer: (a) ITO/Au/ITO, (b) AZO/Au/AZO, (c) TiO₂/Au/TiO₂, (d) Bi₂O₃/Au/Bi₂O₃.
Ellipsometry – modelling

Delta Psi2 Software – Horiba Jobin Yvon
Samples global refractive index $n$, for single layer oxide on glass and three layers oxide/metal/oxide layers on glass substrate (experimental - dots and fit - line)
Transmission coefficient from spectrophotometric experimental data and ellipsometric calculations models for single and three layers samples.
Double Lorentz and Drude classical oscillators

\[ \varepsilon = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_x)\omega_0^2}{\omega_c^2 - \omega^2 + i\Gamma_0\omega} + \frac{\omega_p^2}{-\omega^2 + i\Gamma_D\omega} + \sum_{j=1}^{2} \frac{f_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j\omega} \]

Kato-Adachi dispersion model

\[ \varepsilon = \varepsilon_\infty + \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4 \]

\[ \varepsilon_1 = \frac{A_0}{E_0^{1.5}} \cdot \frac{2 - \sqrt{1 + \chi} - \sqrt{1 - \chi}}{\chi^2} \]

\[ \varepsilon_2 = -\frac{B_1}{\xi^2} \cdot \ln(1 - \xi^2) \]

\[ \varepsilon_3 = \frac{B_1 \cdot \chi}{E_1 - E - i \cdot \Gamma_1} \]

\[ \varepsilon_4 = \frac{C}{1 - \left(\frac{E}{E_2}\right)^2 - i \cdot \frac{E}{E_2} \cdot \Gamma_2} \]

\[ \chi = \frac{E + i \cdot \Gamma_0}{E_0} \]
New amorphous dispersion formula is a rewriting of Forouhi-Bloomer formula

\[ n(\omega) = n_\infty + \frac{B}{(\omega - \omega_j)^2 + \Gamma_j^2} \]

\[ B = \frac{f_j}{\Gamma_j} \cdot \left[ \frac{1}{\Gamma_j^2} - \frac{(\omega_j - \omega_g)^2}{\Gamma_j^2} \right] \]

\[ C = 2 \cdot \frac{f_j}{\Gamma_j} \cdot (\omega_j - \omega_g) \]

\[ k(\omega) = \begin{cases} 
\frac{f_j(\omega - \omega_g)^2}{(\omega - \omega_j)^2 + \Gamma_j^2}, & \omega > \omega_g \\
0, & \omega \leq \omega_g 
\end{cases} \]

Tauc-Lorentz dispersion formula

\[ \varepsilon = \varepsilon_1 + \varepsilon_2 \]

\[ \varepsilon_2 = \begin{cases} 
\frac{1}{E} \cdot \frac{A \cdot E_0 \cdot C \cdot (E - E_g)^2}{(E^2 - E_0^2)^2 + C^2 \cdot E^2}, & E > E_g \\
0, & E \leq E_g 
\end{cases} \]

\[ \varepsilon_1 = \varepsilon_\infty + \frac{2}{\pi} \cdot \frac{P}{E_g} \cdot \int_{E_g}^{\infty} \frac{\xi \cdot \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi \]
Table 2. Ellipsometric fitting parameters for ITO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer ITO/Dispersion model: double Lorentz + Drude</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>ε₀  ε₆  ω₁  ω₂  Γ₀  Γ₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.21 3.08 5.45 0.51 1.64 -0.37</td>
<td>4.57</td>
</tr>
<tr>
<td>ITO/Au/ITO</td>
<td>2.23 3.38 3.96 1.85 6.64 0.60</td>
<td>7.35</td>
</tr>
</tbody>
</table>

Table 3. Ellipsometric fitting parameters for AZO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer AZO/Dispersion model: Kato-Adachi</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ε₀  E₀  A₀  Γ₀  E₁  B₁  B₁ X  Γ₁  E₂  C  Γ₂</td>
<td></td>
</tr>
<tr>
<td>AZO</td>
<td>4.86 2.09 20.70 1.08 3.71 1.78 0.33 0.26 6.65 3.72 -0.48</td>
<td>1.42</td>
</tr>
<tr>
<td>AZO/Au/AZO</td>
<td>1.54 3.31 13.05 -0.001 3.49 0.15 0.59 0.37 5.90 2.53 2.38</td>
<td>3.98</td>
</tr>
</tbody>
</table>
### Table 4. Ellipsometric fitting parameters for TiO$_2$ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer TiO$_2$/Dispersion model: New Amorphous</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_0$</td>
<td>$\omega_n$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.18</td>
<td>3.58</td>
</tr>
<tr>
<td>TiO$_2$/Au/TiO$_2$</td>
<td>1.59</td>
<td>3.67</td>
</tr>
</tbody>
</table>

### Table 5. Ellipsometric fitting parameters for Bi$_2$O$_3$ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer Bi$_2$O$_3$/Dispersion model: Tauc-Lorentz</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Osc$</td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>1</td>
<td>3.08</td>
</tr>
<tr>
<td>Bi$_2$O$_3$/Au/Bi$_2$O$_3$</td>
<td>1</td>
<td>3.17</td>
</tr>
</tbody>
</table>
Table 6. Ellipsometric fitting parameters for Au films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer Au/Dispersion model: Tauc-Lorentz + Drude</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu_{osc}$</td>
<td>$E_0$ (eV)</td>
</tr>
<tr>
<td>ITO/Au/ITO</td>
<td>1</td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>32.96</td>
</tr>
<tr>
<td>AZO/Au/AZO</td>
<td>1</td>
<td>15.65</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.56</td>
</tr>
<tr>
<td>TiO$_2$/Au/TiO$_2$</td>
<td>1</td>
<td>233.51</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.56</td>
</tr>
<tr>
<td>Bi$_2$O$_3$/Au/Bi$_2$O$_3$</td>
<td>1</td>
<td>8.14</td>
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<tr>
<td></td>
<td>3</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>40.59</td>
</tr>
</tbody>
</table>
### Thin films thickness

#### Table 7. Thin films thickness values determined by profilometry measurements and ellipsometry calculations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>$d$ (nm) profilometry</th>
<th>$d$ (nm) ellipsometry</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ITO</td>
<td>45 ± 2</td>
<td>86 ± 2</td>
<td>4.57</td>
</tr>
<tr>
<td>2</td>
<td>AZO</td>
<td>40 ± 2</td>
<td>46 ± 3</td>
<td>1.42</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$</td>
<td>25 ± 2</td>
<td>17 ± 3</td>
<td>0.56</td>
</tr>
<tr>
<td>4</td>
<td>Bi$_2$O$_3$</td>
<td>120 ± 2</td>
<td>124 ± 2</td>
<td>15.39</td>
</tr>
<tr>
<td>5</td>
<td>ITO/Au/ITO</td>
<td>45 ± 2/7 ± 2/45 ± 2</td>
<td>45 ± 2/9 ± 2/43 ± 3</td>
<td>7.35</td>
</tr>
<tr>
<td>6</td>
<td>AZO/Au/AZO</td>
<td>40 ± 2/10 ± 2/40 ± 2</td>
<td>27 ± 1/14 ± 2/22 ± 1</td>
<td>3.98</td>
</tr>
<tr>
<td>7</td>
<td>TiO$_2$/Au/TiO$_2$</td>
<td>30 ± 2/7 ± 2/30 ± 2</td>
<td>21 ± 8/3 ± 2/16 ± 3</td>
<td>3.51</td>
</tr>
<tr>
<td>8</td>
<td>Bi$_2$O$_3$/Au/Bi$_2$O$_3$</td>
<td>120 ± 2/10 ± 2/120 ± 2</td>
<td>141 ± 3/7 ± 1/149 ± 2</td>
<td>6.38</td>
</tr>
</tbody>
</table>
Individual films refractive and extinction index
Optical gap calculations from spectrophotometry measurements
## Optical gap

**Table 8.** Oxide thin films optical band gap values determined by spectrophotometry measurements and ellipsometry calculations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>$E_g$ (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Spectrophotometry</td>
<td>Ellipsometry</td>
</tr>
<tr>
<td>1</td>
<td>ITO</td>
<td>3.80</td>
<td>4.20</td>
</tr>
<tr>
<td>2</td>
<td>AZO</td>
<td>3.48</td>
<td>3.48</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$</td>
<td>3.20</td>
<td>3.58</td>
</tr>
<tr>
<td>4</td>
<td>Bi$_2$O$_3$</td>
<td>2.81</td>
<td>3.08</td>
</tr>
</tbody>
</table>
Electrical properties

The electrical resistivity is of $8 \times 10^{-4} \, \Omega \cdot \text{cm}$ for ITO/Au/ITO, $2 \times 10^{-3} \, \Omega \cdot \text{cm}$ for AZO/Au/AZO, $7 \times 10^{-3} \, \Omega \cdot \text{cm}$ for TiO$_2$/Au/TiO$_2$, $3 \times 10^{-2} \, \Omega \cdot \text{cm}$ for Bi$_2$O$_3$/Au/Bi$_2$O$_3$. 

\[ \omega_p^2 = \frac{4\pi\sigma}{\varepsilon_0 \varepsilon_\infty \langle \tau \rangle} \]
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Dr. A. Stanculescu, Dr. M. Socol, INFIM, Bucharest
Prof. D. Mardare, Prof. L. Leontie, “Al.I.Cuza” University, Iasi
Dr. M. Kompitsas, Nat. Phys-Chem. Inst., Athènes

Professors
Prof. L. Alexandru, Iasi
Prof. M. Rusu, Univ. Al.I. Cuza
Prof. Gh. Rusu, Univ. Al.I. Cuza
Prof. M. Ignat, Univ. Al.I. Cuza

Plateforme XRD
IE. R. Mallet
Prof. N. Mercier
IE. Magali Allain

Plateforme SCIAM
IE. R. Mallet

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L. Hrostea, M. Boclinca

Acknowledgments: COST Action:
Solutions for Critical Raw Materials under Extreme Conditions
Maria Luiza Grilli, Maria-Letizia Ruello
Thank you for your attention