

Physics of Transition Metal Oxides

Lecture 12

Transparent conducting oxides

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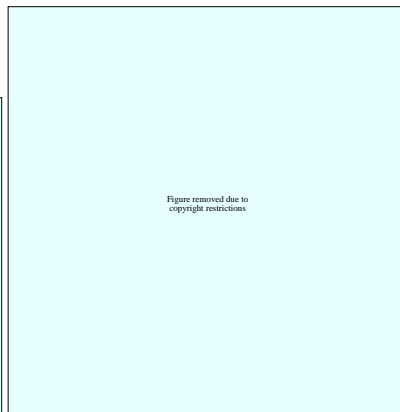
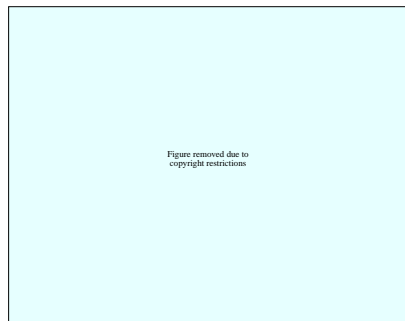
Transparent conducting oxides (TCO):

This is an unusual group of materials, because we get relatively good conductivity and optical transparency in the visible range at the same time.

There is actually only little overlap with transition metals (Cu, Zn). Most TCOs are post-transition metals.

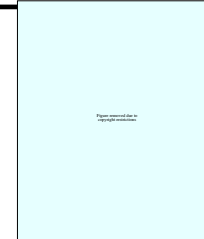
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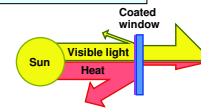


There are two major applications: flat-panel displays and low-emission windows.

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Low-emission windows allow visible light through while reflecting infrared. This keeps the heat out in summer, or the heat in in winter. This is achieved by a thin conducting layer on or in between glass panes. Windows use mostly F-doped SnO_2 .



Common materials for flat panel applications are based on $\text{In}_2\text{O}_3:\text{Sn}$ (ITO). Used for electrodes, touch screens, heaters, shielding, etc.

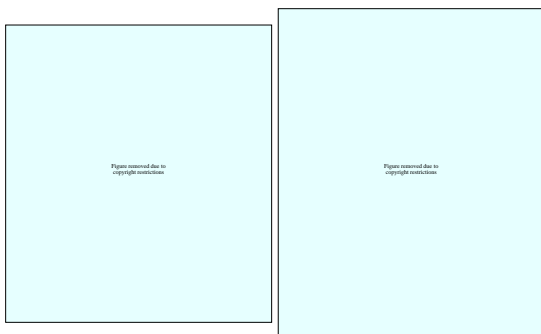
In general, the traditional group of materials used to build transparent conducting oxides include SnO_2 , In_2O_3 , ZnO (doped with F or Al), and CdO . Problems: In oxides are volatile, Cd is poisonous. Several binary oxides are also unstable, CdO convert to $\text{Cd}(\text{OH})_2$, In_2O_3 converts to $\text{In}(\text{OH})_3$ at less than 150°C , SnO_2 absorbs water as in $\text{SnO}_2 \cdot \text{H}_2\text{O}$.

More complex materials are being developed: Cd_2SnO_4 , Zn_2SnO_4 , MgIn_2O_4 , $\text{CdSb}_2\text{O}_6:\text{Y}$, ZnSnO_3 , GaInO_3 , $\text{Zn}_2\text{In}_2\text{O}_5$, $\text{In}_4\text{Sn}_3\text{O}_{12}$.

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Tin oxides (bulk)

SnO_2 is tetragonal ($a=4.737\text{\AA}$, $c=3.186\text{\AA}$). SnO is also tetragonal with $a=3.802\text{\AA}$ and $c=4.836\text{\AA}$. SnO_2 is an extrinsic defect semiconductor. "Pure" SnO_2 usually has a carrier concentration of 10^{17} to 10^{18} and Hall mobilities in the 50 to $200\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ range. Band gap is $\approx 4\text{ eV}$ and the donor activation energy estimates vary from 80 to 750 meV .

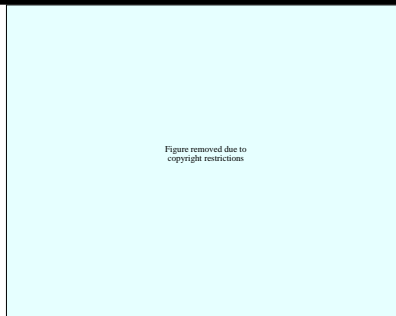


SnO_2 behaves as a traditional extrinsic semiconductor.

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Flat panel displays require better materials than $(\text{InSn})\text{O}_2$, with lower resistivity but low absorption in the visible range.

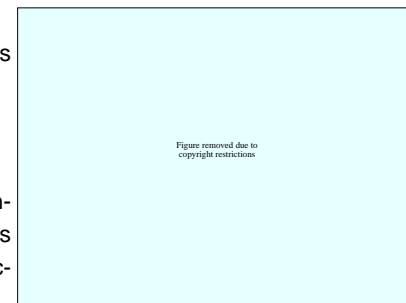
The figure shows the absorption spectrum of ITO films with different sheet resistances. The band-edge absorption cut-off is at the same place. The plasma edge shifts.



Remember what determines the plasma frequency:

$$\omega_p^2 = \frac{Ne^2}{\epsilon_{\text{opt}}\epsilon_0 m^*},$$

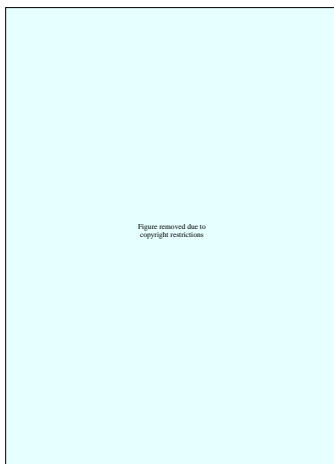
where N is the carrier density, m^* is the effective mass and ϵ_{opt} is the optical dielectric constant.



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The Drude model



To understand the transmission (or reflectivity) of TCOs close to the plasma edge, in the infrared region, Drude model works quite well. (See also lecture 7 notes). The Drude model predicts that the dielectric function is complex ($\epsilon_r = \epsilon_1 + i\epsilon_2$) and

$$\epsilon_1 = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

$$\epsilon_2 = \frac{\gamma}{\omega} \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

where ϵ_∞ is the high-frequency (i.e. visible range) dielectric constant (real) and $\hbar\gamma$ is a relaxation energy. When comparing to our earlier Drude model discussion, $\gamma = 1/\tau$ where τ is the relaxation time between electron scattering events.

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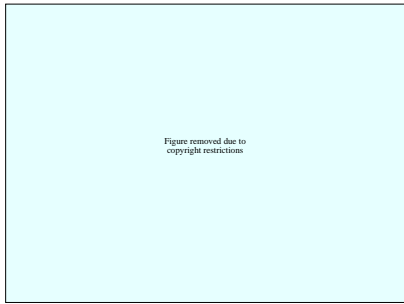
In general it is better to improve mobility than increase carrier concentration to get a good TCO. Increased carrier concentration will lead to larger absorption and may **decrease** mobility due to new scattering mechanisms (additional dopants). Mobility is given by

$$\mu = \frac{e\tau}{m_c^*}.$$

Increasing τ is difficult, because it depends on extrinsic issues (crystal quality). Another choice is to reduce the effective mass, m_c^* . This can be done by finding a better compound (which can have similar crystal quality, i.e. τ).

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Ternary TCOs



Another Sn-based TCO material is Cd_2SnO_4 . Absorption in the visible range is lower than SnO_2 due to a lower carrier concentration. Despite the lower carrier concentration, resistivity is actually lower due to a much higher mobility of carriers.

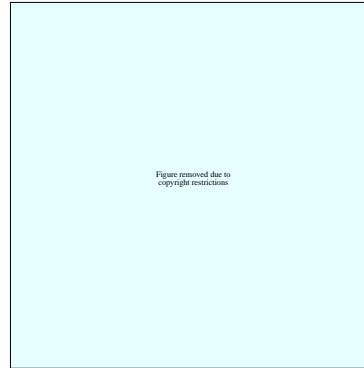
Typical transport numbers are:

Property	SnO_2	Cd_2SnO_4
Carrier density n	$5 \times 10^{20} \text{ cm}^{-3}$	$3.2 \times 10^{20} \text{ cm}^{-3}$
mobility μ	$15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	$54 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
resistance R	$16.7 \Omega/\square$	$7.2 \Omega/\square$

Some of the best TCO result have been obtained in $\text{CdO}:\text{In}$, but this is of little practical value because Cd is toxic.

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The UV side



The carrier densities are

A $0.4 \times 10^{20} \text{ cm}^{-3}$

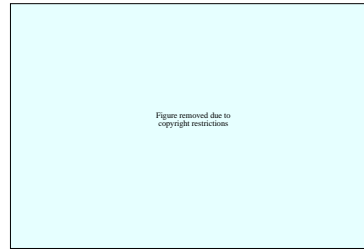
B $1.7 \times 10^{20} \text{ cm}^{-3}$

C $6.2 \times 10^{20} \text{ cm}^{-3}$

D $8.0 \times 10^{20} \text{ cm}^{-3}$

The band gap shifts to higher energy with increasing carrier concentration. This is a common feature for heavily doped In_2O_3 . Normally for moderately doped semiconductors we might approximate the absorption edge with

$$\alpha = \sqrt{\hbar\omega - E_g}$$

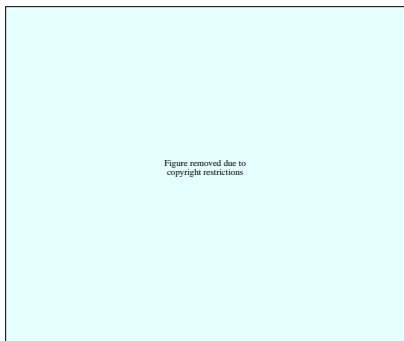


Quite clearly, this is not a valid approximation here. The lowest levels of the conduction band are already full in a heavily-doped material and the Fermi level shifts into the conduction band. The absorption edge therefore shifts to higher energies as the carrier concentration increases (and the conduction band fills more).

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Several processes compete here:

- The lowest levels in the conduction band are blocked, causing a widening of E_g .
- Electron-electron and electron-impurity scattering decrease the gap. That is why $W < E_{g0}$.
- The effective masses are not constant. There is a linear dependence between carrier concentration and effective mass.



Considering only the first mechanism, the gap energy is given by

$$E_g = E_{g0} + \Delta E_g^{\text{BM}},$$

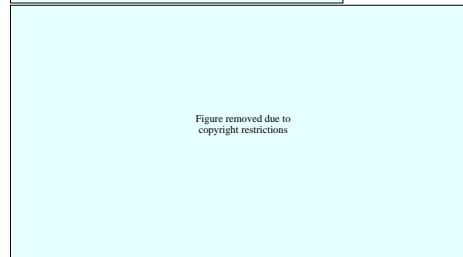
where ΔE_g^{BM} is the Burstein-Moss energy shift, given by

$$\Delta E_g^{\text{BM}} = \frac{\hbar^2}{2m_{vc}^*} (3\pi^2 n_e)^{2/3}$$

The plot shows data for a CdO thin film sample.

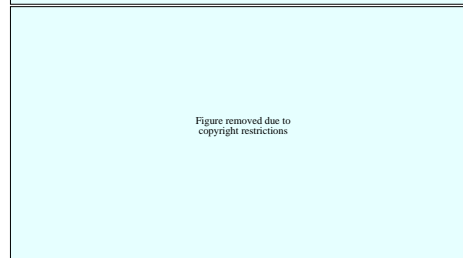
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In_2O_3 has the bixbyite structure. Essentially cubic, but with oxygen vacancy ordering either along a face diagonal (In_2) or along a cube diagonal (In_1).



Calculated band structure of undoped In_2O_3 . Gap is around 1 to 1.5 eV (depends on lattice constant), smaller than the experimental value of about 3.6 eV.

Top of the valence band is made up of hybridized O 2p and In_2 5d states, bottom of conduction band is hybridized O 2s and $\text{In}_{1,2}$ 5s.



$\text{In}_2\text{O}_3:\text{Sn}$

A second gap opens due to strong hybridization between O and In. Dispersion in the s band is slightly reduced, corresponding to a drop in mobility (as is observed experimentally).

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To get a good TCO, we need

- A highly dispersed and single character s -band at the bottom of the conduction band.
- A separation between this band and the valence band that puts the absorption edge in the UV range.
- The plasma frequency should be in the IR range. The frequency drops when the band splits, as in $\text{In}_2\text{O}_3:\text{Sn}$.

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In_2O_3 is usually grown at low temperature in an amorphous form. The amorphous material will start to crystallize at about 150°C

The images shown here are TEM images of as-deposited ITO (a) and annealed ITO at 162°C for 1 h.

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During annealing the resistivity gradually drops. This drop is mostly due to an increase in carrier concentration, rather than change in mobility.

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Another useful starting point is ZnO, doped with various other elements. Common dopants are Al, In, Ga, B, Si, Ge, Ti, Zr, Hf, Sc, Y, etc. Most of the doped films have resistivities in the $10^{-4} \Omega \text{ cm}$ range. Achievable optical parameters are: refractive index $n \approx 2$ and transmittance above 85% in the visible range ($\text{ZnO}:\text{Al}$, $\text{ZnO}:\text{Ga}$).

At low dopant concentrations the mobility is limited by grain boundary scattering.

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A potential barrier is associated with the grain boundaries. The barrier height depends on the structure of the boundary and, for example, on how much oxygen stoichiometry at the boundary deviates from the bulk material.

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Some of the ZnO tilt boundary structures are shown in the figure. The structure changes with angle. Different potential barriers would also be expected for different boundary structures.

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At higher dopant concentrations, the mobility in ZnO is limited by ionized impurity scattering (the Brooks-Herring theory). Each impurity is assumed to create a local potential $V(r) = e^2/er$. The scatterers are assumed to be independent, and here it is also assumed that the conduction band shape is not parabolic. This is a common feature for TCOs, as shown here Cd_2SnO_4 .

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p-type TCOs

Wide-gap materials like TCOs are usually thought of as insulators. This is common for an ionic crystal. Donors also tend to be quite deep and charges localize easily. It is, however, interesting to look for conducting wide-gap oxides, especially *p*-type oxides. These could be combined with the better-known TCOs (all are *n*-type) in *pn* junctions (transparent electronics!).

The TCOs that we have looked at so far, have a ns^0 electronic configuration. We now look how to design a *p*-type TCO.

The first problem is the localization of introduced holes (on oxygen sites) in a strongly ionic compound. Localization effects can be reduced if we can choose a material with a more covalent bonding of oxygens.

The second problem is to select the most suitable cations and a suitable crystal structure.

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The energy levels:



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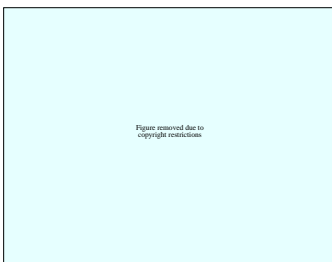
First we need a cation with a closed *d*-shell. This prevents *d* – *d* transitions, which would create absorption bands in the visible range. Refer to lecture 8:

Compound	Band gap (eV)	<i>d</i> – <i>d</i> transitions (eV)
Cr ₂ O ₃	3.3	2.1,2.6
MnO	3.6	2.2,2.9,3.5
FeO	2.4	1.2
αFe ₂ O ₃	1.9	1.4,2.1,2.6,2.9
CoO	2.6	1.1,2.0,2.3
NiO	3.8	1.1,1.8,3.2
Y ₃ Fe ₅ O ₁₂	3	Many

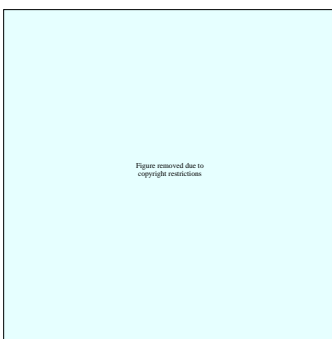
To get a covalent bond, we need to have the cation *d* levels at about the same energy as the O 2*p* levels. The antibonding orbital between the metal and the oxygen will be the highest occupied orbital.

We can consider two closed-shell configurations: $d^{10}s^0$ (Ag⁺, Cd²⁺, In³⁺, Sn⁴⁺, Sb⁵⁺) and $d^{10}s^2$ (In⁺, Sn²⁺, Sb³⁺). No *p*-type TCOs have been found in the $d^{10}s^2$ group so far.

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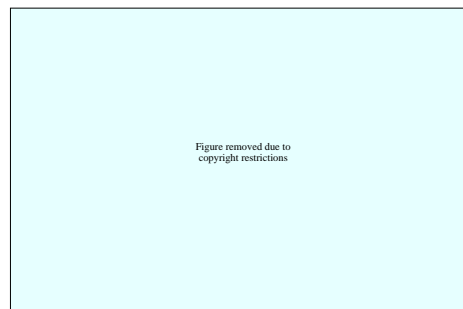
A photoemission spectrum of CdIn₂O₄ spinel shows that it is indeed an *n*-type semiconductor with the Fermi edge close to the conduction band bottom. The gap width is about 3 eV. The conduction band top consists of O 2*p* levels. About 7 eV below oxygen is the Cd 4*d* peak and 6 eV below that comes the In 4*d* peak.



In general, atomic energy levels shift to lower energy with increasing atomic number, as shown here for 3*d* and 4*d* elements. This data applies to free ions, but the relative shifts should apply roughly to ions in a lattice as well. The Cd-In shift is about 6 eV, consistent with the UPS result. The plot shows that Ag⁺ levels should almost overlap with O 2*p*. Same arguments apply to Cu⁺.

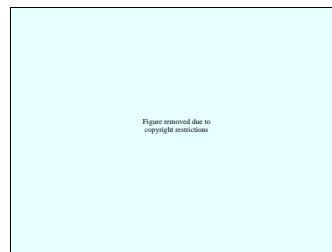
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We also need a suitable crystal structure to get the desired metal-oxygen bonding. One possible candidate is the delafossite structure. The general formula is AMO₂, where A is a monovalent cation and M is a trivalent metal ion. The structure is layered and hexagonal. The A-O distance is relatively large and there is no oxygen in the A layer. This should reduce repulsion problems between the closed shell of the A cation and oxygens, hopefully keeping the energy levels aligned.



Indeed, *p*-type conductivity has been found in this system. Examples are CuAlO₂ and CuGaO₂. The band gap is around 3.5 eV for both materials.

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The resistivities of CuAlO_2 (●) and CuGaO_2 (○) are similar; semiconducting at higher temperature and a hopping mechanism at lower temperatures. The activation energy is about 0.2 eV. Room-temperature conductivity is not good, $9.5 \times 10^{-1} \text{ S cm}^{-1}$ in CuAlO_2 and $6.3 \times 10^{-2} \text{ S cm}^{-1}$ in CuGaO_2 , much worse than the $0.9 \times 10^4 \text{ S cm}^{-1}$ achieved by ITO. The Hall mobilities follow the resistivity data, giving $10.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for CuAlO_2 and only $0.23 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for CuGaO_2 .

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This plot shows that the Seebeck coefficient is also positive (CuAlO_2), i.e. this is indeed a *p*-type material.

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Another *p*-type TCO candidate is SrCu_2O_2

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The Cu^+ ions are in zig-zag chains and only interact with oxygens within these chains. Conductivity can be modified by doping with potassium.

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Room-temperature conductivity is still very low, only $4.8 \times 10^{-2} \text{ S cm}^{-1}$. Band gap is 3.3 eV.

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Another strong candidate for use as a *p*-type TCO is doped ZnO. ZnO is intrinsically an *n*-type material due to oxygen vacancies and Zn interstitials in the lattice.

Doping the lattice with N should give a *p*-type material. Unfortunately there is a strong repulsion between the N dopants, making this difficult. Also, the carriers introduced by the dopants, are localized.

Codoping with N and Ga is expected to produce a highly-doped *p*-type oxide. In this case the dopants form a N-Ga-N cluster, leaving an extra hole, stabilizing the dopants in the lattice and, probably, allowing the extra holes to delocalize.

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n and *p*-type TCOs can be used to build transparent devices. This image shows the transmission spectrum of a *pn* junction and a photo of the device. The device consists of ZnO/*n*-ZnO/*p*-SCO/ITO layers. The junction is formed by the *n*-ZnO and *p*-SCO layers. ITO and ZnO are electrodes.

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The junction works as a (slightly leaky) diode.

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Low-emissivity windows: The plasma frequency is set at around $2 \mu\text{m}$ in cold climates to let the Sun's radiation in and also keep the long wavelength IR radiation inside. In hot climates the IR cut-off is set at $\approx 1 \mu\text{m}$ to keep the heat out. Windows use often metal layers (silver or TiN), enclosed between glass sheets to protect the metal layer.

Solar cells: Usually based on $\text{SnO}_2\text{:F}$, which gives the best conductivity. On plastic substrates both ITO and ZnO can be used.

Flat-panel displays: The layer needs to be patterned by etching. ITO is therefore used, although tin oxide would give better conductivity. ITO can also be grown at low temperatures to cover the organic color filters. ZnO will be used in the future.

Electrochromic mirrors and windows: Based on two $\text{SnO}_2\text{:F}$ layers with an organic electrochromic layer sandwiched between them. Used mostly in car rear-view mirrors.

Defrosting windows: The first TCO application during in military airplanes to defrost the windows. Originally used SnO_2 , now mostly ITO. Largest use in supermarket freezer windows. Car windows often use metal alloys sandwiched between glass layers. ITO cannot be used because the resistivity is too high for a 12V power supply.

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Oven windows: New grills and ovens have a window for looking in. The glass surface should reflect IR to keep the oven hot and the window cool. Coatings must be thermally stable, mostly using SnO_2 .

Static dissipation: Used to cover copy machine glass plates and CRT tubes to remove static charge. Mostly SnO_2 .

Touch-panel controls: Coatings need to be very durable, resistivity is not critical. Common choice is SnO_2 .

Electromagnetic shielding: Coating of windows to prevent electromagnetic radiation from escaping (computer safety).

Invisible circuits: Security circuits on windows and museum display cases.

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