

## Transparent Electronics

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**Abstract:** Transparent electronics is the next level of technology that the world requires. It is a technology which helps in producing invisible electronic circuits and optoelectronic devices. Numerous applications can be built upon transparent electronics which would change the style of the world we are living in today. The applications contain consumer electronics such as transparent windows which would sense the trespassing and would send a message to the owner of the house regarding the intruding action of someone, transparent windshields, electronic spectacles similar to Google glass, e-Wear or e-Skin etc. However the materials for such type of technology must be transparent and also possess the conductivity characteristics which are quite contradictory. Transparent conductors are neither 100% optically transparent nor metallically conductive. But some of the compounds have been discovered which possess these two properties to a satisfactory extent. And the research of such materials is still going on.

The key performance metrics of transparent thin film transistors would be high device mobility and low temperature fabrication. Generally high device mobility enables fast device operation and low power consumption, which broadens the application area of TFTs. On the other hand, low temperature fabrication is essential for transparent devices made on flexible substrates which would enable novel applications. Low temperature fabrication also lowers the fabrication expense significantly. Despite the above mentioned success, the reported mobility values are still low compared to those of non-transparent devices indicating further room for improvement.

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### I. Introduction

Conductors cannot be completely optically transparent and metallically conductive. This can be understood by better understanding why some materials are transparent while others are not. Neither inter- nor intra-molecular bonding types (vanderwaals, ionic, covalent, metallic bonding) play a minor or major role in deciding the transparency of the material. In the end, the dielectric function will theoretically define the reflectivity, transparency, absorption of a solid for a specific wavelength of light for these types of bonding (ionic / electronic polarization).

Transparency is mainly determined by the free electrons, position of Fermi energy and type of band structure in a solid. Electrons in solids occupy so called bands, separated by a gap. The band gap is also known as HOMO/LUMO gap. This is an energy range in a solid where no electron states can exist between the Highest Occupied Molecular Orbital (HOMO), and the Lowest Unoccupied Molecular Orbital (LUMO). Electrons occupying the same band have the same energy. The arrangement of electrons on the different energy levels is an important factor for the transparency and opacity of materials. Electrons can move to other band absorbing (or losing) energy amount equal to band gap. If the band gap size is in the same range as energy of photons of visible light, such photons are absorbed by electrons so they can't pass through the solid. Such solid is not transparent. If the band gap is smaller or larger, visible light can go through the solid not absorbed and the solid is transparent. Of course the main specific bonding types in a semiconductor will co define Fermi energy, band structure. But they are necessary, not sufficient factors for optical properties of solids.

The porosity and the grain boundaries of a material also play a vital role in the transparency of the material. However, Rubies and other gemstones based on Al<sub>2</sub>O<sub>3</sub> clearly are transparent. The product is actually composed of millions of tiny crystals, where the interface (known as grain boundaries) between these acts to scatter light photons. If you heated the piece up enough, and grew those tiny crystals to larger and larger crystals, the part would eventually become transparent. Rubies are a single crystal, with no boundaries or porosity (trapped air bubbles) so they do not scatter light. For example say glass, if we grind up glass to powder and then cook the particles together, the pieces would not be transparent. Again if we melt the particles together long enough to get rid of porosity and grain boundaries, it would be transparent.

Transparency also relates to the actual material and the photons which can be absorbed by the crystals. Metals absorb most incident light radiation because their electrons easily absorb this energy. That's why most metals are grey. Germanium is added to fiber optic glasses, because Ge does not interact with Infrared photons to the extent Si does. More Infrared photons are transmitted as a result. So structure/bonding nature does play an

important role however, it is also dependent upon processing/impurities/surface finish. Anything can be transparent if made thin enough.

An insulator consists of completely filled valence and empty conduction bands; whereas metallic conductivity appears when the Fermi level lies within a band with a large density of states to provide high carrier concentration. Most commonly used transparent conducting oxides (TCO) are  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{CdO}$ . These are insulators with optical band gap of about 3eV. To become transparent and conducting, these hosts must be degenerately doped to place the Fermi level up into the conduction band. Since most of the electrons are already placed into the conduction state, it leads to low optical absorption and also high mobility of extra carriers. The Burstein-Moss (BM) shift helps in broadening the optical transparency window and in keeping the intense optical transitions from the valence band out of the visible range. This is critical in oxides which are not transparent throughout the entire visible spectrum, for example, in  $\text{CdO}$  where the optical band gap is 2.3eV.

Greater the number of carriers in the oxide leads to good conductivity but also in poor transparency. Thus finding a balance between the transparency and conductivity is a challenging task because of the complex relationship between the electronic and optical properties.

Exclusively oxides of the post transition metals with  $(n-1)d^{10}ns^2$  electronic configurations are considered, which have densely packed structures with four or six coordinate metal ions. Strong interactions between the oxygen 2p and metal ns orbitals give rise to electronic band structures qualitatively similar for all these oxides. The band gaps are made primarily of occupied 2p antibonding bands and unoccupied dations bonding bands for valence band maximum and conduction band minimum. The bonding O 2p states form the valence band while the non bonding O 2p states form the conduction band. These interactions result in a gap between the valence and the conduction bands. In  $\text{ZnO}$ , the gap is direct while is indirect in  $\text{CdO}$ ,  $\text{In}_2\text{O}_3$  or  $\text{SnO}_2$ .

For carrier generation, these oxides need to be doped to introduce the carriers in the oxide hosts transforming them into transparent conducting oxides. Substitutional doping and Oxygen Reduction are the methods by which the doping can be carried out.

Doping with aliovalent ions is the most widely used approach to generate free carriers in TCO hosts. Generally, same period next row elements e.g.  $\text{Sn}^{4+}$  for  $\text{In}^{3+}$  and  $\text{In}^{3+}$  for  $\text{Cd}^{2+}$  are used as dopants. However other dopants may prove to be beneficial for optimizing[9 the properties for specific applications. Transition metal dopants offer the possibility to enhance conductivity via an increased mobility (due to smaller BM shift) of the free carriers and not their concentration.

Removal of oxygen atom from a metal oxide leaves two extra electrons in the crystal. In light metal oxide, the oxide free energy of formation is high and oxygen vacancies create deep charge localized states within the electronic band gap known as F centres or Colour centres. Relatively low oxide free energy of formation of conventional TCOs favours large oxygen deficiencies giving rise to free carrier densities. Band structure investigations of oxygen deficient oxides reveal that the oxygen defect corresponds to non-conducting state regarding to the filling of the single conduction band. If the vacancy induced electrons are excited via photo excitation or partially compensated, does the single conduction band become half occupied and conducting behaviour may occur. The presence of oxygen vacancies leads to significant changes in the band structure of a TCO host.

Compared to substitutional doping, oxygen reduction of TCO host may result in higher carrier densities but would limit the electron mobility. Thus substitutional doping is the preferred method of doping in conventional TCO hosts.

Multi component TCOs containing a combination of In, Zn, Cd and Sn metal ions widen the range of TCO materials for various applications. Single cation TCOS have anisotropic electron effective mass whereas multi component TCOs have isotropic electron effective mass. Even then no multi component oxide has never outperformed the conventional single cation TCOs due to the challenges of doping. Substitutional doping becomes difficult as the number of multi valent cations increases owing to the same valence substitution. However many of these limitations can be overcome in the amorphous state of these oxides.

## II. Fabrication of ideal TCO:

Introduction of a deep impurity band with a high density of states in the band gap of an insulating host material would help to keep inter band transitions above the visible range. This requires the band gap of a host material to be more than 6.2eV. In addition, the impurity band should be narrow enough ( $<1.8\text{eV}$ ) to keep intra band transitions as well as the plasma frequency below the visible range. To achieve high conductivity, the concentration of impurities should be high enough so that their electronic wave functions overlap well to form a band.

To fabricate such an ideal TCO, a material with a close packed structure may not be suitable, because the required large concentration of impurities would result in increase of ionized impurity scattering which limits electron transport. Zeolites are considered to be potential candidates for such ideal TCOs. This class

of materials possess the desired structural and optical features namely spacious interconnected pores and large band gaps, as well as exhibit the ability to trap functional guest atoms inside the nanometer sized cavities which would govern the transport properties of the material.

### III. Transparent amorphous oxide semiconductors

The most important feature of semiconductors is in the controllability of carrier concentration over several orders of magnitude. An advantage of amorphous materials over crystalline materials is their capability of large area deposition of uniform thin films at low temperatures. This makes amorphous semiconductors extremely favourable for large sized electronic devices fabricated on plastic substrates and hence is preferable for flexible electronics.

Transparent amorphous oxide semiconductor thin film transistors have high field mobility, large and are easily fabricated at low temperature using conventional DC sputtering. By annealing at an appropriate temperature far below the crystallization temperature of transparent amorphous oxide semiconductors, the performance of TFTs fabricated under unoptimized conditions can be improved.

### IV. Driving backplane of OLED and Liquid Crystal Display (LCD) panels

Conventional active matrix (AM) flat panel displays are based on amorphous or polycrystalline silicon TFT technology. Due to the optical absorption and low field mobility of the amorphous silicon (a-Si), pixel aperture and driving ability is less for some applications. Luminous intensity of OLED is proportional to the flow current for which higher mobility TFTs are required. Although polycrystalline silicon TFTs have larger field effect mobility, its uniformity over large area limits the electron transport and also is not acceptable for high yield manufacturing. In recent years, there has been more emphasis on TFTs made of TOSs. This is mainly due to the advantages such as visible light transparency, a large area uniform deposition at low temperature and high carrier mobility.

### V. P-type transparent semiconductors

Realizing p-type materials is a complicated task mainly because the mobility of carriers in the valence band is lower than that of carrier in the conduction band as in the case of n-type conductivity. p-type conduction is associated with carrier movement through a valence bond. Few inorganic materials have been demonstrated to exhibit the necessary electronic and structural features for effective p-type doping. Inorganic p-type transparent semiconductors are found among oxides, chalcogenides, nitrides, silicides and others. Much recent attention has focussed on Cu-based semiconductors, of which delafossite family  $\text{CuMO}_2$  ( $M = \text{Ga, In, Sc, Y}$ ) is the primary oxide example. There is also a growing research on carbon based electronics, particularly nanotubes which may prove to be important in transparent electronics.

There are transparent heterojunctions with rectifying characteristics. The rectifying behaviour is not the evidence for a true bipolar junction because this can also be seen in Schottky diodes. A transparent homojunction reported is a Cu based oxide ( $\text{CuInO}_2$ ). The junction exhibits rectifying I-V characteristics with a turn on voltage of 1.8V. The more promising hole mobility in the chalcogenides is offset by the lack of corresponding n-type semiconductors in similar materials.

Transparent oxide semiconductors were created from transparent conductive oxides. The current status of TOSs is far from the ideal situation, in particular for carrier polarity control. Although many papers have reported p-type TOSs, including p-ZnO, no p-channel TFTs with a field effect mobility of  $>0.1 \text{ cm}^2(\text{Vs})^{-1}$  had been realized by 2007. It is considered that instability or high gap state density is the primary reason.  $\text{Cu}_2\text{O}$  is a well-known p-type semiconductor and was used as the active layer since the first TFT in 1935. In 2008, was reported a p-channel TFT with a mobility of  $1.4 \text{ cm}^2(\text{Vs})^{-1}$  employing SnO (not  $\text{SnO}_2$ ) as the active layer. This is the first demonstration of a p-channel oxide TFT with a mobility  $>1 \text{ cm}^2(\text{Vs})^{-1}$  which was a long standing target. Attempts were made to fabricate p-type conduction in PbO where  $\text{Pb}^{2+}$  has a  $6s^2$  electronic configuration but were unsuccessful.

Wide band gap p-type semiconductors are used in light emitting diodes (LEDs), light sensors and even lasers. Thus, these semiconductors might be incorporated into transparent circuits as well as being useful photonic elements independent of transparent circuitry. P-type wide band gap semiconductors may be the most important elements for solar cells. Highly conductive, highly transparent semiconductors are commonly used for passive applications where transparency is critical. These might include heat reflecting window coatings, contacts for touch screens, and heating elements for windshields or windows on refrigerated displays. P-type materials with larger effective masses and relatively large carrier concentrations having plasma edges that are tunable in the infrared may find applications in IR – transparent electronics.

The materials used as wide gap p-type semiconductor systems:

- I. Cu oxides:  $\text{CuAlO}_2$ ;  $\text{CuMO}_2$  where  $M = \text{Ga, In, Sc, Y}$  (delafossite structure)

- II. Binary Oxide: ZnO, NiO
- III. ZnRh<sub>2</sub>O<sub>3</sub>; p-type spinels
- IV. BaCuChF, LaCuOCh, BaCu<sub>2</sub>S<sub>2</sub> (Chalcogenides, Chalcogenide Fluorides, Chalcogenide Oxides)
- V. Carbon Nanotubes

## VI. Carbon Nanotubes

Carbon nanotube (CNT) thin films have been successfully incorporated as both high quality semiconductor layers and electrodes in large area flexible, transparent electronics. Semiconducting CNT thin films are transparent, flexible, environmentally stable and possess higher field effect mobility than organic semiconductors. The highest mobility demonstrated in a TFT comes from a p-type material in the form of a single wall Carbon Nano Tube (CNT).

To realize high performance p-type TTFTs with high mobility, carbon nanotubes are considered as their intrinsic mobility is over 100,000cm<sup>2</sup>/Vs, good mechanical flexibility and good optical transparency. Random nanotube networks were used as active channels for TTFTs but the best obtained mobility was ~30 cm<sup>2</sup>/Vs. This low mobility might result from the fact that electrical conduction in a random nanotube network has to go through many nanotube-nanotube junctions. Aligned carbon nanotubes which can directly bridge source and drain are therefore expected to offer better performance.

Conventional transparent, conducting films (e.g. ITO) have been used as electrodes materials in organic TFTs but due to expensive growth techniques and inherent brittleness make these materials incompatible with flexible electronics. Solution processed CNT thin films are optimized to achieve sheet resistance and transparency that are comparable to ITO, as well as being more flexible than ITO. Thus, CNT thin films have been independently utilized as high quality active components and as electrodes.

Transfer printing methods are used to pattern and assemble monolithic carbon nanotube (CNT) thin film transistors on large area transparent flexible substrates. A transfer printing method was used to pattern the semiconducting CNT thin film without exposure to any processing chemicals while an airbrushing method was used to produce the CNT thin film electrodes. Gate leakage in printed CNT TFT devices was avoided by engineering an organic / inorganic hybrid dielectric. An Al<sub>2</sub>O<sub>3</sub>/poly-methylmethacrylate (PMMA) dielectric bilayer was used to achieve a minimal gate leakage. CNT based devices on a polyethylene terephthalate (PET) substrate exhibit field effect mobilities in the range 1 – 33 cm<sup>2</sup>/Vs and on/off ratios up to 10<sup>4</sup>. In contrast to p-type control devices, these CNT based devices show ambipolar behaviour which could be useful in complementary circuits.

As in the reference [], flexibility of air brushed CNT thin films. PET stripes coated with airbrushed CNT thin films were wrapped around cylinders of varying diameters to induce tensile strain. According to the above, the sheet resistance starts changing at r = 10mm, but changes only by 7% when the substrate is bent to r = 2mm. Multiple bending tests were also performed and sheet resistance changed only by 12% after bending to r = 2mm for 35 times. Bending the devices further, r <6mm resulted in gate leakage. Thus, the PMMA/Al<sub>2</sub>O<sub>3</sub> bilayer acts an effective diffusion barrier of CNTs under significant strain.

All the CNT bottom gate devices, whose electrodes are also CNT, show ambipolar behaviour with hole conductivity up to an order of magnitude greater than electron conductivity. In contrast, Au contact control CNT bottom gates show p-type behaviour.

## Conclusion

Understanding the principles of the conventional transparent conductors provides a solid foundation for further search of novel TCO host materials as well as efficient carrier generation mechanisms to make them good conductors. If oxide-based C-MOS structures can be fabricated on various types of substrates, including plastics, flexible electronic circuits would be promising. By using a novel process, Stanford and Nebraska-Lincoln researchers created thin-film organic transistors that are five times as fast as existing organic transistors. They have reportedly shown that it is possible to make organic transistors that are 90% transparent to the human eye. But transparent electronics still requires a process that can create reliable circuitry at low costs.

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