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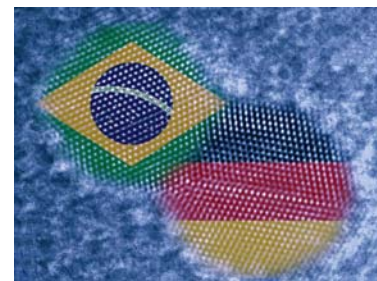
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Transparent, conductive oxides for coating applications

Mario Quilitz, Peter W. de Oliveira, Sabine Heusing, Michael Veith

Transparent, conductive oxides (TCOs) applied as coatings find multiple applications in various areas such as flat panel display setups, as electrodes in touch-screen panels, electrochromic devices, solar cells and in architectural applications for example as IR reflectors.

The favored material in the class of TCOs is still ITO – Sn-doped In_2O_3 – due to its unique combination of high transparency and electrical conductivity. Though already very good, the potential of the ITO coatings with regard to their conductivity leaves some space for future improvements. Also ITO as a material has some serious drawbacks, such as limited availability and high costs. This work presents some strategies to overcome these obstacles.

One way to enhance the conductivities of alternative materials is to use carbon nanotubes as a dopant. This strategy was tested for ATO (Antimony-doped Tin Oxide), Titan dioxide and AZO (Aluminium-doped Zinc oxide). The results for these materials are presented.

In coatings of ITO on glass or polymeric foils usually silica-based binders are used. They have the disadvantage to reduce the contact between the highly conducting grains and thus reduce overall conductivity in the composite. The matrix between the nanoparticles can be improved by several measures. Experiments with relevance in this direction are discussed.

A third strategy aims at the reduction of costs in the process of ITO fabrication. Here one way to go is to use an electrochemical synthesis method. Results of the line of development are presented.

Other strategies comprise the suitable processing of materials with a lower intrinsic conductivity or the search for materials with high intrinsic conductivity close to that of ITO. Examples are presented and discussed.

Transparent conductive oxides for coating applications

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1. Introduction

Transparent conductive oxides (TCOs) an unusual combination of material properties as they are on one hand provide highly electrically conductive and on the other hand show high optical transmission as well. Usually glasses or ceramics are known for high optical transparency and metals for high electrical conductivity. The combination of both properties is rare and restricted to a comparably small group of materials. Therefore, when used in coatings, TCOs find multiple applications in various areas such as electrodes in touch-screen panels or for other flat panel display setups [1-5], in electrochromic devices [6-8], in photovoltaics [9,10], for electromagnetic shielding [11,12] or for gas-sensing [13,14].

A forthcoming area comprises the application in OLEDs for lighting. As lighting consumes about 25 % of the global electrical energy, the replacement of energy saving lamps by OLEDs has a huge potential for saving energy. The OLEDs require transparent conductive electrodes. Here TCOs can be used [15-17].

Low emissivity coatings are an interesting issue in architecture. Instead of letting the heat generated by infrared radiation into the room after passing the window glass, the infrared radiation with wavelengths beyond 2 μm is reflected directly at a layer coated onto the window glass thus reducing the need for climatization in the room. This is an item especially in tropic countries where a big amount of electricity is used for climatization. Here transparent conductive oxides such as ITO can be used as IR reflectors [18,19].

The favored material in the class of transparent conductive oxides is still ITO – Tin-doped indium oxide – due to its unique combination of high transparency and electrical conductivity. The processing of a typical TCO material can be illustrated using the example of ITO, indium tin oxide. ITO is synthesized via a precipitation from a solution which means by a controlled growth process. After calcination and reduction processes, a powder of Tin-doped Indium oxide with an average grain size of 20 to 30 nm is obtained. By addition of suitable surface modifiers and solvents a suspension is produced, which can be used to manufacture coatings. Application of the coatings is performed usually by means of wet chemical coating techniques. While smaller samples (up to 10 cm x 10 cm) are prepared via spin coating or bar coating, larger samples are coated via dip- or roll-to-roll processes. Curing of the coatings depends on the substrates to be coated. While coatings on substrates like glass can be cured thermally, coatings on polymeric substrates have to be cured by UV- or IR-irradiation which normally requires the addition of suitable photo initiators.

As the latter techniques allow coating on polymer foils it was only natural to use printing techniques for the coating of foils. Printing techniques have many advantages: They are easily up-scalable, allow continuous processing and direct patterning without any etching or other additional structuring processes and – last but not least – provide a cost efficient method of application. With all these features the process is suitable for the production of printed electronics.

When the physical properties of the various coatings are compared - especially for the conductivities - one observes big differences between those prepared on polymeric substrates and those prepared on glass where the conductivities are higher by one order of magnitude. The difference is even higher if films are compared to pellets made of chemically synthesized indium tin oxide. While films made by chemical processes rarely exceed conductivities of 1 Scm^{-1} , with sintered pellets conductivities up to more than 1000 Scm^{-1} can

be achieved [20]. This remarkable difference, a gap of three orders of magnitude, raises the question what – if the pellets can be considered as the upper limit of conductivities obtainable for chemically synthesized samples – causes the low conductivities in the films.

If one only looks at the isolated nanoparticles, their intragranular conductivities are comparable. Therefore it can be assumed that the intergranular conductivities are causing the above mentioned differences. In the case of the films there are always binder phases present to keep the nanoparticles together and in case of the films on polymeric substrates additional photo starters are needed to initiate the curing process. The binder phases are usually silica based systems e. g. MPTS (methacryloxypropyltrimethoxysilane), a bifunctional organosilane. The role of this compound as a binder phase is at least three fold: First, it “glues” together the nanoparticles, second, it provides adhesion of the film to the substrate and in its third role it gives mechanical stability to the composite film. Though already very good, the potential of the ITO coatings with regard to their conductivity leaves some space for future improvements. Here especially the matrix between the nanoparticles can be improved by several means.

This work provides some strategies to overcome the above mentioned obstacles. Some results will be shown and discussed.

Other problems are associated with the mainly used material, indium tin oxide. Despite of many parallel activities ITO is still the premiere material of choice. Nevertheless it has several serious disadvantages. Among the most severe drawbacks, the first is the possible future inavailability which is due to the worldwide limited reservoir of indium containing minerals. Sooner or later the material will not be available at a reasonable cost which will not only create a shortage of the resources but will cause an imponderability in the process of the manufacturing. The other main drawback closely related to the first are the high costs of indium tin oxides which is now about 2500 € per kg.

The strategies to overcome the material and system obstacles introduced above comprise four main lines:

The first line to improve the conductivities in TCO materials aims at enhancing the conductivity by doping. This means that materials with lower intrinsic conductivities are doped by suitable conductive materials to achieve an enhanced overall conductivity of the respective composite. In the long range the conductivities obtained by this or any other method or by combining various approaches, have to be in the range of the conductivities of indium tin oxide. Here the use of carbon nanotubes as dopants proved to be useful. This first route is established for several systems. i.e.: ATO (Antimony doped tin oxide, $\text{SnO}_2 : \text{Sb}$), titania (TiO_2) and AZO (Aluminum doped zinc oxide, $\text{ZnO} : \text{Al}$). Results were reported and discussed. An outlook on further strategies will be given.

The second strategic line comprises the enhancing of the matrix conductivity by modifications of the matrix phase. Here the binder phase is the main focus of the work. For this second route first results indicate a remarkable feasibility. The first material system was successfully tested as a matrix conductivity improving material.

In a third line of strategy alternative routes of synthesis for ITO were investigated. They can partially replace ITO in its expensive forms by the use of cheaper educts and processes. Here some work was already performed. It will be described and results will be discussed.

Finally a fourth line aims at enhancing the intrinsic conductivity of alternative materials. This implies as a rule the search for suitable processes to enhance the intrinsic conductivity. However it can also include the search for new alternative materials as replacements for indium tin oxide. Compared to the other strategies this line requires much more basic work and the thorough investigation of many physicochemical, structural and microstructural aspects of the selected materials. This line up to now is investigated only to a minor extent which is due to its high complexity.

2. Experimental

Enhancing of conductivity by doping:

As already mentioned the first route is established for several systems. i.e.: ATO, TiO₂, and AZO. Preparation includes the precipitation of nanoparticles from precursors and the formation of a suspension. This suspension is combined with a suspension containing the functionalized CNTs. Resulting sols are usually stirred, ultrasonicated and microfluidized subsequently. Coatings were usually prepared by spin-coating on a borofloat glass. Curing respective sintering procedure depends on the substrates and process history. Due to lack of space experimental details are described elsewhere: For ATO processes are described in more detail in [21, 22]. For TiO₂ and AZO more details are found in references [23, 24] and [25] respective.

Enhancing the matrix conductivity:

For the second route first test results indicate the principle feasibility. The first metal oxide (M_nO_m) system was tested as a matrix conductivity improving material. Preparation includes the precipitation of nanoparticles from precursors and the forming of a suspension. To this suspension the dopant components are added in partial substitution of the binder phase. Resulting sols are used to prepare coatings by spin-coating on borofloat glass or by other coating techniques such as gravure printing on polymeric foils. Curing and sintering procedure depend again strongly on the substrates and process history. Due to lack of space the experimental details will be described elsewhere [26-27].

Alternative routes of synthesis for indium tin oxide:

Alternative routes of synthesis for ITO can partially lead to the replacement of expensive precursors or expensive process steps in the preparation of ITO, thus making the process cheaper.

Various attempts to reduce costs in the conventional forms of synthesis of indium tin oxide nanoparticles or nanoparticulate coatings have been performed.

One alternative described below comprises an electrochemical synthesis from metal electrodes. For the electrochemical synthesis and its experimental details see [20]. Methods for characterization of this samples are also described in this reference.

Enhancing the intrinsic conductivity of alternative materials and search for alternatives to replace ITO:

The search for alternative materials ideally replacing ITO is an ongoing process which was probably started at the time ITO was first used as a TCO. In the search for alternative materials and for processes to alter intrinsic conductivities of the transparent oxide materials many techniques were employed (see e. g. references [28-31]). Due to lack of space it is not possible to describe all the synthesis and characterization techniques used.

3. Results and discussion

Enhancing of conductivity by doping:

In our previous work the route of enhancing the conductivity by doping was established for several systems. These systems include ATO, TiO₂, and AZO. The only dopant tested in this regard are functionalized CNTs. Experiments to compare the effect of CNTs with that of other doping materials are on the way.

Figure 1 illustrates the effect of doping an ATO (antimony doped tin oxide, SnO₂ : Sb) ceramic with carbon nanotubes. The sheet resistivities are shown versus temperature of sintering. The sample with CNT doping is denoted ATO/MWNT because the doping consists of multi-walled carbon nanotubes (MWNT). An effect of reduction of the sheet resistivity by the doping is visible at lower temperatures. Though a clearly significant effect is seen, it is less than one order of magnitude. At sintering temperatures above 300 °C the effect of the doping becomes very small and at temperatures beyond 500 °C the doped samples show

even higher resistivities than the undoped. This is due to the thermal destruction of the nanotubes and presumably the formation of carbon species with no conductivity.

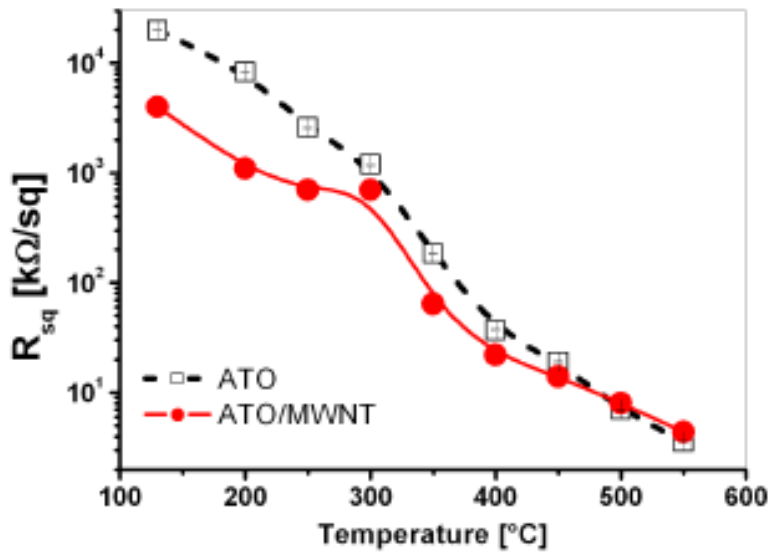


Fig. 1 Comparison of sheet resistances of ATO (antimony doped tin oxide) and ATO doped with CNTs [21].

It is worth noticing, that despite of the reduction of the resistivity, the absolute values of the achieved resistivities are far from being good. This is a consequence of the poor quality of the carbon nanotubes which show non-uniform properties. Also the resistivity of the ATO ceramics are far from optimum.

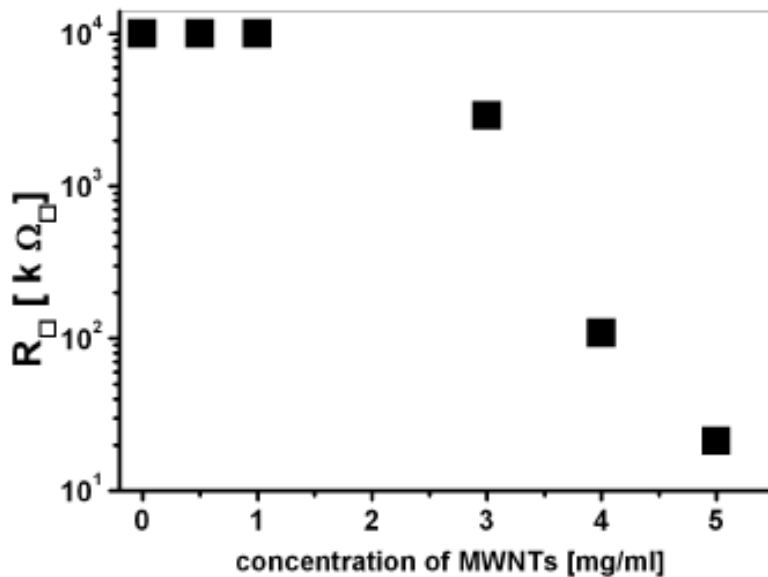


Fig. 2 Comparison of sheet resistances of titanium oxide undoped and doped with various concentrations of CNTs. CNTs are reported as MWNT (multi walled carbon nanotubes) [27].

Attempts to incorporate CNTs in a matrix of titania lead to the results depicted in Figure 2. In these experiments the conditions of sintering are constant. The sheet resistivities are shown versus the concentration of MWNTs in the TiO₂ matrix. Up to a concentration of more than 1 mg MWNTs per ml suspension the resistivities of the composites remain rather constant. At higher concentrations of more than 3 mg/ml the resistivities started to decrease. The

decrease in dependence of the increasing concentration of carbon nanotubes reflects the percolative forming of transport paths in the composite microstructure. With a reduction of nearly three orders of magnitude the effect of the CNT doping is comparably pronounced, but however still the absolute values of the resistivities are too high for application.

The experiments with AZO (Aluminum doped zinc oxide, ZnO : Al) doped with carbon nanotubes are still ongoing. So far values of sheet resistivities of around and below 10^1 k Ω /sq could be obtained with AZO containing coatings.

In tests with carbon nanotubes applied as transparent coatings without an additional ceramic matrix even higher resistivities were obtained. This again points towards non-uniform microstructural features of the commercially produced carbon nanotubes.

Future cooperations with the Brazilian network for carbon materials bear the chance to combine well characterized carbon nanotubes with ceramic composites to obtain better electrical properties.

Enhancing matrix conductivity:

Whenever binder phases are present in a coating to keep the nanoparticles together, to generate adhesion to the substrate or to provide mechanical stability the usually used binder phases are silica based compounds such as MPTS (methacryloxypropyltrimethoxysilane), a bifunctional organosilane. As silica is an insulator the contact between the conductive ITO grains is interrupted and limited to a very small number of conduction paths. Thus especially the matrix between the nanoparticles can be improved by several means. Our strategy comprises the improvement of the matrix conductivity by the introduction of in-situ forming conductive compounds which is incorporated in the composite in partial or complete replacement of the binder. This attempt was successfully evaluated for the first M_nO_m (metal oxide) system. Figure 3 illustrates the results.

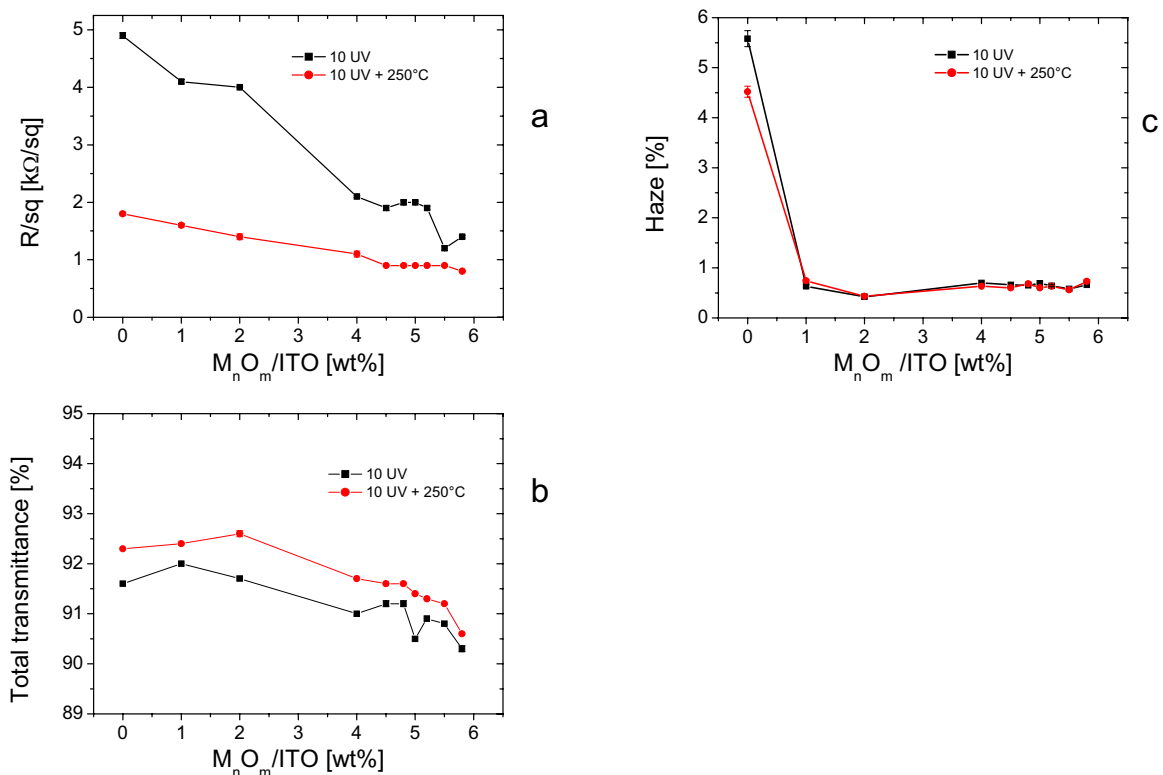


Fig. 3 Partial replacement of the binder phase by a higher conductive phase which is formed in-situ in the matrix leads to various effects on the physical properties. Increasing content of additive metal oxide phase like leads to: a) reduction of the sheet resistance, b) slight reduction of transmission and c) a reduction of haze [26].

The partial replacement of the binder phase by a higher conductive metal oxide phase being formed in-situ in the matrix leads to various effects on the physical properties. An increasing content of the added metal oxide phase first reduces the observed sheet resistance (a). The amount of incorporated replacement material into the binder composition however has some limits: The binding function must not be too much reduced. Also a loss of mechanical stability can only be tolerated up to a certain extent. At higher amounts of additive phase cracks and mechanical deteriorations of the coatings can be observed. The effect of decrease in resistivity on the other hand is not as high as desired but it shows the principle feasibility of the method. The other diagrams (b) and (c) in Figure 3 illustrate the effects on transmittance which is slightly reduced with an increasing additive phase content and on haze which is also reduced. For this effect relatively small amounts between 1 and 2 % of additive phase are sufficient. A side effect of the method is the faster UV hardening of the coatings on polymer foils.

Alternative routes of synthesis for indium tin oxide:

In an alternative process nanoscaled indium tin oxide (ITO, $\text{In}_2\text{O}_3 : \text{Sn}$) was prepared via an electrochemical method from metal electrodes in an aqueous system which contained ammonium acetate as a conductive salt. Figure 4 depicts the set-up for the electrochemical synthesis according to this method.

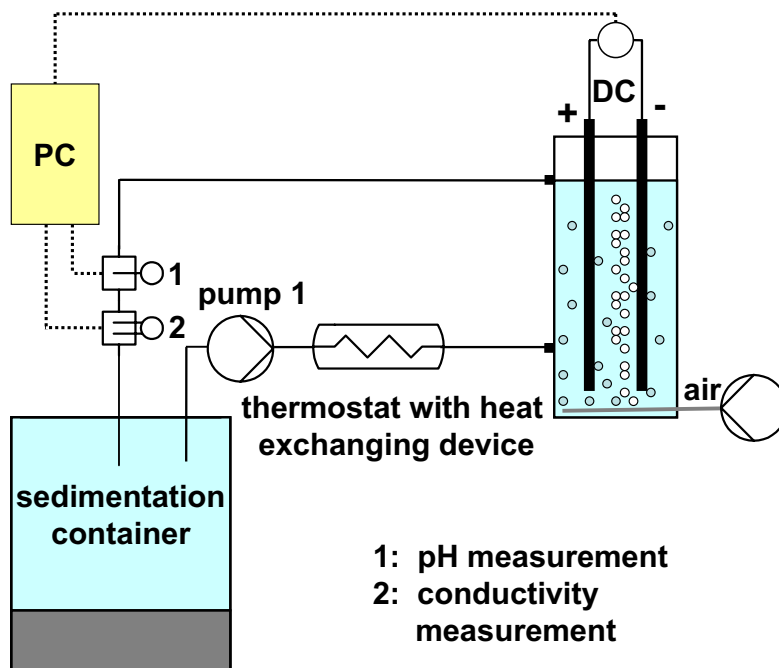


Fig. 4 Set-up for the electrochemical synthesis of ITO via an electrochemical technique [20].

As an intermediate product nanocrystalline $\text{In}(\text{OH})_3$ was obtained which in turn serves as a precursor for the subsequent calcinations and - associated with tin doping - resulted in ITO powders. Depending on the atmosphere the dehydration of tin doped $\text{In}(\text{OH})_3$ started at 150 °C, and a solid solution of cubic ITO was formed between 190 °C and 300 °C. At sintered samples which were post-treated in various ways, electrical conductivities up to 1400 Scm^{-1} were observed.

Enhancing the intrinsic conductivity of alternative materials and search for alternatives to replace ITO:

As mentioned the fourth strategy aims at enhancing the intrinsic conductivity of alternative materials.

It is reasonable to search for suitable processes to enhance the intrinsic conductivity.

Due to the very complex nature of the physical and chemical properties of transparent oxide materials there is a large variety of parameters which influence the combination of optical transparency and electrical conductivity. The resistivity is influenced by the charge carriers, by their concentration and mobilities. The charge carriers depend also on the defect chemistry which sets the equilibria of the defect interactions such as association and trapping of charge carriers, the relation between electronic and ionic charge carriers and so on. Last but not least structural and microstructural parameters strongly influence the resistivities but also the optical properties as transparency, absorption, reflectivity and haze.

Processes which are used to improve the intrinsic conductivity of alternative materials have to take into account all these dependencies. Some promising methods are found in thermal post-treatments, treatments under special atmospheres and other techniques.

The strategy can also include the search for new alternative materials as replacements for indium tin oxide.

In principle four families of TCO materials are known so far. They can be divided either along structural classifications or after the predominant type of electrical charge carriers:

Tetrahedrally-coordinated cations are present in zinc oxide or in AZO (ZnO : Al). These materials are n-type conductors.

Other n-type conductors show octahedrally-coordinated cations like CdO, ATO and SnO₂, CdIn₂O₄, Cd₂SnO₄, and others and form a second family of compounds. The most prominent member of this group however is ITO itself.

There are two other families which comprise both p-type conductors. One family has structures with linearly-coordinated cations. These include the members of the structure type ABO₂, the so called delafossites. A typical example is the TCO compound CuAlO₂.

The fourth family is less common and is built of cage frameworks, like mayenite, which has the composition 12CaO·7Al₂O₃.

So far mostly materials like ITO, ATO and AZO are considered to be good candidates. All of them are members of the n-type families. Clearly, the search should be widened to find other potential TCOs for the future.

4. Conclusion

The most popular material in the class of TCOs is still ITO – Sn-doped In₂O₃ – due to its unique combination of high transparency and electrical conductivity. Though already very good, the potential of the ITO coatings with regard to their conductivity leaves some space for future improvements. Some of the conditions in bindered composite coatings made of nanoparticles and additional phases limit the achievable conductivities. ITO itself is the material of choice due to a lack of other suitable candidates, but it still has some serious drawbacks including limited availability and its high price.

Several strategies to improve the situation are discussed in this article.

An important strategy aimed at the enhancement of the conductivity of alternative TCO materials by doping with carbon nanotubes. Results on ATO, titania and AZO are presented here: However despite principally promising results the absolute values of the achieved conductivities are rather small.

The matrix between the nanoparticles leaves much space for improvement as can be seen from a comparison of coatings and sintered pellets. It can be achieved by a partial replacement of the insulating binder phase by conductive alternatives. The first metal oxide system shows promising but still not sufficient increases in conductivities.

Alternative synthetical methods can reduce costs and supply materials with altered properties. An electrochemical synthesis from metal electrodes is proposed.

Last but not least there is a strategy, to improve the intrinsic conductivities of alternative materials by altered process technologies or to look after new alternative TCO materials.

As stated above especially the latter lines of work will require much more basic work and the thorough investigation of many physicochemical, structural and microstructural aspects of the selected materials. Therefore these areas are investigated so far only to a minor extent due to their very complex nature.

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