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TRANSPARENT CONDUCTING OXIDES: STATUS AND OPPORTUNITIES IN BASIC RESEARCH

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ABSTRACT

In this paper, we begin by discussing the historical background of transparent conducting oxides and then make some general remarks about their typical properties. This is followed by a short discussion of the desired properties for future applications (particularly photovoltaic devices). These are ambitious objectives but they provide targets for future basic research and development. Although it may be possible to obtain these properties in the laboratory, it is vital to ensure that account is taken of industrial perceptions to the development of the next generation of materials. Hence, we spend some time discussing industrial criteria. Next, we discuss key physical properties that determine the macroscopic physical properties that, in turn, affect the performance of devices. Finally, we select several key topics that ought to be included in future basic research programs.

INTRODUCTION

Transparent conducting oxides (TCOs) have been used in several applications for three or four decades but, despite the huge volume of experience in the field, there remain many unanswered questions at both applied and fundamental levels. The reason that these issues have not been addressed, or only superficially so, is largely because the performance of the TCOs has been adequate to meet the demands of most applications considered thus far. For the purposes of the present document, the applications of concern are photovoltaic cells and modules, but the broader range of applications includes transparent electrode materials for both electrochromic cells and for liquid crystal display devices. In the case of both solar cells and the other two applications, improvement in *performance* of the TCOs is important because their non-ideal properties will eventually impact the performance of the complete device. We shall provide a definition of the term *performance* later in this document. From this point, we shall address the specific demands on TCOs imposed by prospective photovoltaic applications.

In the field of polycrystalline thin film solar cells, the dominant materials at present are copper indium gallium diselenide [1] (CIGS) and cadmium telluride [2] (CdTe). In addition, a-Si:H cells depend sensitively on the properties of the TCO transparent

electrode. The first of the above cells is generally known as a substrate device and second as a superstrate device. The practical implication of this distinction is that the TCO element is either deposited directly onto the glass substrate before the absorber layers are deposited, or it is deposited on top of the semiconductor stack after all of the layers have been deposited. Although it is obvious that specific optical properties are required, additional important criteria must be met by the TCO and by the method used for its deposition. We shall discuss these later.

General Observations

During the last thirty to forty years, the dominant TCOs have been tin oxide (SnO_2), indium oxide (In_2O_3), indium tin oxide (ITO), and zinc oxide (ZnO). All of these materials have been mass-produced in very large volumes over a long period of time and we assert that no new TCOs have been developed until about the last 5 years. During this time, there has been substantial coordinated activity in Japan, with Minami being particularly active [3]. Although efforts have been made elsewhere to develop new TCOs with the potential for improved performance [4-8], with the exception of a modest program at NREL from about 1985 onwards, a brief program at AT&T Lucent Technologies in the mid-1990s, and a recent start-up program at Northwestern University, there have been very few concerted efforts in the United States.

The options are simple; to achieve superior performance, the TCO community must either discover new and improved materials or must find better ways of making the conventional TCOs mentioned above. We believe that the first of these is likely to prove far more fruitful than the second simply because of the huge number of publications devoted to optimization of TCO film deposition. It must also be recognized that there is a significant difference in the performance of the best material produced in research laboratories and those produced by manufacturing companies. While it is desirable to improve the performance of both, we must remember that the mass of coated glass (the usual substrate) produced by an average sized float glass melter is on the order of 600 tons/day [9]. Consequently, the deposition rate in large volume manufacture must necessarily be very rapid, compared with that typically used in laboratory R&D. Although we believe that there are many basic research issues that ought to be addressed, we also recognize that the needs of the eventual large-scale manufacturer must be carefully considered.

A TCO is a wide band-gap semiconductor that has a relatively high concentration of free electrons in its conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. The high-electron-carrier concentration (the materials will be assumed to be n-type unless otherwise specified) causes absorption of electromagnetic radiation in both the visible and infrared portions of the spectrum. For the present purposes, it is the former that is the more important. Because a TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between the properties is required. Reduction of the resistivity involves either an increase in the carrier concentration or in the mobility. Increasing the former also leads to an increase in the visible absorption. Increasing the mobility, however, has no deleterious effect and is

probably the best direction to follow. To achieve a high-carrier mobility will necessarily improve the optical properties. As we shall re-emphasize later, we see this as a key direction for future research and development of TCOs.

In present day, thin-film solar cells, both high- and low-resistivity materials are required to achieve maximum efficiencies. The role of the high-resistivity layer may be less obvious, but it appears that it is needed to prevent shunts of the junction leading to loss in voltage and fill factor. Optimization of the properties of TCOs generally requires an elevated temperature at some point in their fabrication. For example, some materials are deposited onto very hot substrates, which is compatible with glass manufacture, but some must be deposited onto heat-sensitive substrates such as plastics. For the latter, the upper limit on deposition or annealing temperature is probably less than 200°C. In addition, in the CIGS substrate cell, zinc oxide is the last layer deposited, and its deposition temperature must be compatible with the semiconductor layers already deposited. If the TCO deposition temperature increases much above 250°C, then interdiffusion of layers can occur, thereby ruining the device performance.

Required Properties

At the start of a potentially new part of R&D into photovoltaics, it is necessary to define goals. The properties of TCOs that come most readily to mind are the electrical sheet resistance and the optical transmittance. These will be considered initially. However, other properties are likely to become very important to manufacturers of cells and modules and we shall discuss those later in this section.

To a first approximation, we may suggest that a proper emphasis on novel TCOs should lead to a resistivity of less than $10^{-4} \Omega \text{ cm}$ (corresponding to a sheet resistance of less than $2 \Omega / \text{G}$ for a film $0.5 \mu\text{m}$ in thickness), together with maximal transmittance in the visible part of the spectrum. Although a sheet resistance of less than $10 \Omega / \text{G}$ and a transmittance of greater than 80% in the visible part of the spectrum, may be acceptable for present-day solar cells, a more ambitious, more carefully defined target must be provided for future programmatic efforts. The definition of the desired electrical properties is straightforward but the definition of the optical properties needs more care. The reflectance and/or transmittance of thin TCO films exhibit interference fringes in the visible and, although the transmittance may peak at a value of 85-90%, this is probably not a realistic average across the operational spectrum of typical devices (approximately $0.4\text{--}1 \mu\text{m}$). If instead, we define an absorption coefficient, this would be physically more useful. So, for example, if we have a film $0.5 \mu\text{m}$ in thickness and its absorption coefficient is $2 \times 10^3 \text{ cm}^{-1}$ or less, then absorption will be a minimal problem. However, this performance should, ideally, be maintained across the entire operational wavelength range. Thus, a target of resistivity of $5 \times 10^{-5} \Omega \text{ cm}$ and a visible-absorption coefficient, due to free carriers, of $2 \times 10^3 \text{ cm}^{-1}$ or less are well beyond those achieved by any research laboratory and would be a difficult but feasible goal for a sustained, well-funded research program. In addition, these criteria must be met for a material with a band gap of at least 3 eV.

Ideally, we would need a mobility of at least $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to achieve these properties, and, in our opinion, it is on this quantity that the future research must focus. Typical mobilities of conventional semiconductors are generally less than $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, although there have been reports of higher values being achieved for cadmium stannate (Cd_2SnO_4) [10].

In the next section, we shall comment on some industrial requirements that must also be met. If the novel materials developed by the R&D community are to be acceptable to industrial manufacturers of cells and modules, these need to be carefully considered. We shall continue by presenting a series of rhetorical questions concerning the key issues of charge scattering, the role of impurities and defects, and materials. We shall also include some input from theoreticians, which may be useful in seeking for new TCOs with potential applicability.

INDUSTRIAL CONSIDERATIONS

In its roadmap for the future, the glass industry has made it clear that they expect the manufacture of photovoltaic modules eventually to become a major product of the glass industry [9]. However, this is not presently the case. Assuming, however, that the roadmap prediction is realized, then one can appreciate that an extremely rapid rate of deposition must be used in order to handle the very large areas leaving the glass melter per unit time. Both sputtering and chemical vapor deposition, (CVD) can accommodate very large areas, and both can be designed for rapid rates of deposition. Of the two methods, CVD, probably has the lower capital cost and it is capable of producing mechanically tough films of large areas and acceptable (for present applications) electrical and optical properties. Film deposition may only take about thirty seconds to be compatible with the rate of deposition projected to be used in the manufacture of CdTe solar cells [11].

If sputtering emerges as the preferred deposition technique, then either metallic or metal oxide targets may be used. Metal targets are almost certainly cheaper to manufacture, but have a significant problem associated with them. In particular, during reactive sputtering, nodules tend to form on the target surface. These distort the distribution of the electric field across the surface and make the rate of erosion (and, consequently, the deposition rate as well) somewhat erratic. Progress has been made towards finding a solution to this problem by target manufacturers, who have used very dense sputtering targets. Nevertheless, the problem remains to some extent. If oxide targets are used, then these have their own problems. First of all, radio-frequency sputtering must be used. This is more expensive, more hazardous, and has a slower rate of deposition than CVD. The targets themselves are typically manufactured by pre-reacting stoichiometric mixtures of the individual oxides and then pressing these into targets. Occasionally, target suppliers manufacture hot-pressed targets that consist simply of the mixed oxides. The oxide targets are more expensive and present the issue of recycling. Although it is straightforward to reprocess a metal target, the same cannot be said of an oxide target.

Target manufacturers, particularly those of metal targets, are very sensitive to issues concerning toxicity. Even though the amount of toxic material (cadmium, for example)

in a TCO film is very small, the perspective of the target manufacturers concerns the machining of the targets themselves and the need to protect machine operators (and ultimately the company itself) from the toxic metals therein. Strict safe operating procedures must be imposed and these represent cost, which clearly must be recovered through sales, thereby leading to higher target costs. Consequently, the issue of target toxicity is of great concern to the target manufacturers rather than to the end users of the TCO films.

The end-user of the TCO film, i.e., the cell/module manufacturer, will certainly demand that the film is readily amenable to etching or patterning, and must be simple to scribe with a laser. Chemical etching is problematic for tin oxide and this must be taken into account in the future development of novel TCOs.

The surfaces and interfaces of TCOs sometimes need to be smooth, as is the case with the CdTe and the CIGS solar cells, or hazy, i.e., textured, as is the case for α -Si:H cells. The indirect band gap of the amorphous materials requires the films be textured to increase the path length through the absorber layer, thereby enhancing optical absorption. With CdTe and CIGS, the materials have direct band gaps and texturing is unnecessary. The interfaces of the TCO and other layers of the devices, e.g., CIGS, CdTe or CdS, must be stable and must also have a low-specific contact resistance. Film deposition sometimes requires an elevated substrate temperature. For a substrate cell, this will not affect the semiconductor layers to be deposited subsequently. This may not be the case for superstrate cells for which deposition and elevated temperatures may be necessary after all other semiconductor layers have been deposited. The performance of cells is usually dominated by interfacial regions and these must be carefully controlled. The contact resistance issue is not so severe because it is relatively easy to achieve values of less than some specified maximum permissible value (say, $10^{-2} \Omega \text{ cm}^2$) or, when this is not the possible, other aspects actually dominate the parasitic losses in the device, as seems to be the case with the CdTe cell.

Finally, it is very likely that in mass production, manufacturers will accept critical production windows. Ideally, the deposition conditions must be reasonably forgiving and not require sensitive control.

BASIC RESEARCH QUESTIONS AND OPPORTUNITIES

In this section, we shall discuss some fundamental questions that must be answered if the projected performance figures defined earlier are ever to be realized. As was pointed out, the development of future TCOs must pay very careful attention to maximizing the carrier mobility. The first sub-section will raise a number of questions concerning the scattering processes. In many cases, the origin of the free carriers in TCOs is not clear. In some TCOs, defects such as oxygen vacancies may be responsible for the carriers. However, the donor-like oxygen vacancies must lie at rather shallow levels to give such high-carrier concentrations. Hence, the second sub-section deals with questions concerning defects and impurities. In the next sub-section, we raise some questions concerned specifically with materials.

The Nature of Charge Scattering Processes

As mentioned above, the search for, fabrication of, and analyses of new TCO films must focus on achieving materials with higher electron mobilities. This can only be achieved by making material with longer electron relaxation times (i.e., by permitting the electrons to travel further between the successive randomizing collisions) or by identifying materials with lower electron-effective masses. It was pointed out long ago that attempts to increase the carrier relaxation time may prove fruitless because so many researchers, using many different deposition techniques, in the last thirty years or so have adjusted their deposition parameters to give optimal material. However, there has never been a clear example of a new deposition method, or set of deposition parameters, that led to significantly higher values of mobility than are usually reported. It was for this reason that our own investigations of cadmium stannate were first commenced. [5]. This material was pioneered by Nozik [10] and coworkers [12] in the early 1970s and it was suggested that the significantly higher mobilities achieved may have been associated with lower electron-effective masses. Although we have now achieved comparable mobilities, our detailed analyses of the transport properties indicate that the effective masses are similar to those reported for other TCOs. Coincidentally, however, the material does appear to lend itself to improved deposition techniques and the achievement of significantly higher values of relaxation time [13]. To this extent, we obtained the right result for the wrong reason! Despite this, we still suggest that an appropriate role for solid-state theorists would be to construct band diagrams and estimate effective masses of likely new TCOs identified on the basis of other theoretical criteria. Ionized impurities have often been identified as the likely scattering centers, but in very few cases have steps been taken to prove this assertion. In our own work, we have used the so-called *method of four coefficients* [14] in which the conductivity, Hall coefficient, Seebeck coefficient, and Nernst coefficient, are measured on the same sample without any change in the configuration. This enables not only the effective mass and the relaxation time to be calculated directly, but also gives the scattering parameter that relates electron relaxation time to Fermi energy. This work has also established that the conduction band is parabolic to within experimental uncertainty. Additional theoretical work is needed to show that this is expected from ab initio arguments.

In polycrystalline materials, it is often presumed that grain boundaries scatter charge carriers and cause a reduction in mobility relative to single crystals. Potentially, the grain boundaries may be effective scatterers of charge but, in reality, we do not believe that this is necessarily the case. For a heavily degenerate semiconductor, the electron mean-free path is on the order of 4 nm. This is much less than typical grain sizes leading us to the tentative conclusion that grain boundary scattering is probably unimportant. We have also never observed a significant variation with frequency of the ac impedance of the film, lending further support to the notion that the grain boundaries are shunted. Finally, the degeneracy of the material (i.e., the energy separation between the Fermi level and the conduction-band minimum) can be as high as 0.7 eV, which is probably larger than the height of the grain boundary potential barrier. For these three reasons, we have reached the conclusion that grain boundaries are probably unimportant in TCO films. However, this requires separate confirmation, and we encourage other researchers in the field to test this hypothesis. It would be interesting, for example, to work at lower carrier concentrations for which grain boundary scattering may be expected to play a much

stronger role, and to compare its behavior with theories of grain boundary scattering [15] and scattering by ionized impurities [16], neutral impurities [17] and other mechanisms.

At high electron concentrations, (10^{20} – 10^{21} cm⁻³) it is highly probable that compensation will occur. So far as we are aware, this has not been taken into account in any assessment of TCOs. This is, therefore, an important direction for future theoretical and experimental investigation.

Finally, at high-electron concentrations, screening of impurity ions will likely occur. The positively charged ions gather a cloud of electrons around them, thus restricting their electric field to the immediate vicinity of the cloud. Calculations of the role of screening have been made that suggest higher mobilities may be achievable than have been predicted to date on the basis of ionized impurity scattering alone. Hence, future theoretical investigations of charge transport should include the role of both compensation and ionized impurity screening. If one discounts the role of grain boundaries as a scattering species, then we must address the role of ionized impurities or some other mechanism.

If scattering occurs within the grains rather than at the grain boundaries, then it is important to identify the mechanism of scattering. If dislocation networks form, then it is important to know how they act electrically and whether their contribution may be reduced by improved fabrication methods. As mentioned earlier, it has often been speculated that oxygen vacancies give rise to the free electrons in the conduction band of the TCOs. This raises the interesting question of whether high mobilities could be achieved in stoichiometric films extrinsically doped. Examples of extrinsically doped TCOs include zinc oxide and tin oxide doped cationically with aluminum and antimony respectively, and anionically with fluorine. Nevertheless, exceptionally high mobilities have not been observed, although the films may not have been precisely stoichiometric. Our own work on cadmium stannate has led to high mobilities (relative to other TCOs) and these films have been made without extrinsic doping. Although our results are promising, in reality we know neither the source of the carriers nor the dominant scattering mechanism [13]. It would be interesting to investigate cadmium stannate and, perhaps, other materials in the spinel family using extrinsic doping to establish the mobility at even higher carrier concentrations. This, of course, presumes that compensation does not overwhelm the additional donors.

Single crystals of several TCOs have been made [18-21] and very much higher mobilities have been demonstrated than have ever been achieved in thin polycrystalline films. Although the temptation is to conclude that the difference is due to grain boundary scattering, for the reasons outlined above, we are inclined to discount this possibility. It appears to be more likely that the increased mobility is due to improved material quality. That being the case, it may still be possible to improve the quality of polycrystalline TCOs, thereby increasing their mobility. However, single crystal TCOs need to be manufactured in order to support these studies. The crystals should be large enough to permit characterization using the standard techniques but, in addition, we believe that a wider range of characterization techniques may be required. The crystal sizes, therefore, need to be amenable to these. The four coefficient method used at NREL, for example, requires minimum areas of approximately 7x3 mm. Most work on single crystal growth

has led to samples that are dendritic and very difficult to characterize electrically and optically.

The Nature of Defects and Impurities

In summary, there are many interesting and potentially valuable avenues of research open to much more detailed research and development than has been conducted on TCOs in their history to date.

As discussed earlier, the origin of the electrons in unintentional doped TCO films is far from clear. Although many papers state that these are associated with oxygen vacancies, it is perhaps surprising that these lie at shallow levels, relative to the conduction-band minimum, rather than at deeper levels as is found for other native defects in other semiconductors. With most semiconductors, it is more efficient to dope stoichiometric material extrinsically rather than relying on the native defects. Although this has been done in ZnO:F and In₂O₃:Sn, extrinsic doping has not been used with most TCOs and particularly those developed recently. Therefore, we recommend that some attention be paid to the deliberate doping of TCO films. This could be performed during film deposition or subsequent to deposition with the former preferred.

MATERIALS

In the CdTe superstrate cell, the incident light passes first through the glass substrate, next to the TCO film, and then into the p-CdTe/CdS layers of the junction itself. Exactly the same happens with a-Si:H cells. In both cases, therefore, a reverse-bias junction between the n-type TCO and the p-type absorber layer must be formed, and the properties of this may affect the performance of the device to a greater or lesser extent. However, the extent is unknown, but incorporating a p-type TCO at the front surface could solve this problem. However, except for one or two notable exceptions, there have been no reports of successful fabrication of p-type materials. Given the inverse dependence of the mobility on effective mass, one may expect that the electrical and optical performance of p-type TCOs to be inferior to those of n-type films with their much lower electron effective masses. However, all this needs to be determined by both theory and experiment, and we suggest that this work is urgently needed.

The subject of co-doping has been discussed in the literature during the last one to two years, and it has had very interesting effects that may be useful in the development of p-type TCOs. There are some notable examples of materials being doped with a carrier type opposite to that which is normally observed. For example, high conductivity n-type diamond films have been made by Nishmori et al. [22] and p-type GaN was made by Yamamoto et al. using either Be or Mg acceptors with either Si or O as the donor co-dopants [23]. Yamamoto et al also proposed using the co-doping approach for the production of p-type CuInS₂ [24]. In the present context, it is also interesting to note that Yamamoto et al proposed to use the co-doping method for the fabrication of p-type ZnO [25] This work was, however, theoretical and so far as we are aware, has not yet been

reduced to practice. We suggest that systematic studies of the use of co-doping in the fabrication of p-type TCOs be initiated. Given their potential advantages, this is a topic we chose to emphasize later in the next section, dealing with key recommendations. First, we shall deal with some general criteria that may be useful in searching for new and improved TCOs.

As implicit in the name, viable transparent conductors must be simultaneously transparent and conducting, an unusual combination. To date, this combination has only been usefully realized in a limited class of metal oxides, all of which yield n-type conductors. By comparing a variety of known materials we can establish some general guidelines that may be useful in searching for new transparent conductors, possibly including p-type transparent conductors and non-oxide transparent conductors.

Stoichiometric In_2O_3 is a transparent insulator that can be doped by substituting Sn for In to yield n-type indium tin oxide (ITO), a well-known transparent conductor. In contrast, Al_2O_3 , which is isoelectronic with indium oxide and is another transparent insulator, can not be effectively doped. A major difference between these two materials is that In is a multivalent cation as evidenced by the existence of several indium oxides: In_2O_3 , InO and In_2O . In a simple integer-valence ionic model, the In valence increases from +3 to +2 to +1 in this sequence. Hence, the multivalent nature of In likely enables the In_2O_3 host electronic structure to accommodate the enormous conduction electron concentrations (of order $10^{20}/\text{cm}^3$ or more) typical of useful transparent conductors, and associated with the three indium oxides mentioned above.

Considering only the multivalence cation criterion, one might expect WO_3 to be an excellent TCO host. Stoichiometric WO_3 is transparent, with a nominal W valence of +6. Compounds with tungsten ion valences of +6, +5, +4, +3 and +2 are generally considered stable. However, when WO_3 is electron doped with either oxygen vacancies or Li intercalation to form Li_xWO_3 , the film quickly darkens. Hence, its use in electrochromic devices. WO_3 can accommodate high-conduction electron concentrations but does not remain transparent. The multivalency is therefore not a sufficient condition for a material to form a TCO.

Again, considering a simple integer-valence ionic model, tungsten in WO_3 has electronic configuration W^{6+} : $[\text{Xe}]4f^{14}5d^06s^0$ whereas indium in In_2O_3 has electronic configuration In^{3+} : $[\text{Kr}]4d^{10}5s^05p^0$. Hence, adding electrons to W^{6+} adds electrons to the energetically clustered 5d levels, whereas adding electrons to In^{3+} adds electrons to the empty 5s and 5p levels. Of course, substantial metal/oxygen hybridization occurs but, in general, adding electrons to energetically clustered bands will probably introduce optical transitions in the visible portion of the spectrum. Hence, for n-type transparent conductors, the conduction band minimum should be well separated energetically from higher lying bands. This condition is met in the elements Cd, In, Sn, Zn and Ga, all of which still have filled d-bands after reaction with oxygen.

It is also important that anion vacancies act as shallow donor levels, rather than as deep traps. In alkali-halides, anion vacancies yield electron traps that are deep enough for transitions between the conduction band and the traps to occur, with associated absorption bands, in the visible. Similar absorption bands exist in alkali-earth metal

oxides such as CaO, SrO and BaO. Not only can such spatially localized electrons yield coloring optical transitions, but they will also not yield metallic conduction.

The preceding discussion considered only n-type materials. However, p-type transparent conductors would be very useful for the reasons given earlier. Actually, conducting p-type metal oxides are very well known; almost all copper oxide-based, high-temperature superconductors are p-type conductors derived from semiconducting hosts such as La_2CuO_4 , which has a band gap of about 2eV. However, these materials and many other stoichiometric transition metal oxides, are correlated electron insulators, rather than filled-band insulators. Not only do these materials generally become broadly absorbing when doped, but even when perfectly stoichiometric, sub-band-gap optical excitations exist due to coupled vibrational, magnetic, and excitonic transitions. Hence, correlated electron insulators are not potential host materials for transparent conductors.

Suggestions have recently been made that two other copper oxide-like materials may be p-type transparent conductors. These are CuAlO_2 and SrCu_2O_2 . Both of these are p-type transparent thin films that have been successfully made, but with carrier densities of order $10^{17}/\text{cm}^3$: much lower than n-type materials. It is interesting to consider these two materials in light of the preceding discussion. Again, considering a simple inter-valence ionic model, the Cu ion is Cu^{1+} : $[\text{Ar}]3d^{10}4s^0$, in both materials, making these materials filled d-band insulators, rather than correlated electron insulators. Furthermore, two copper oxides are well known, Cu_2O (Cu^{1+}) and CuO (Cu^{2+}). Hence, in CuAlO_2 , the multi-valent cation criterion may imply that the material can accommodate p-type doping. However, adding holes to Cu^{1+} adds holes to the Cu d-states, which is analogous to adding electrons to WO_3 and leads to strong absorption. There are two possible explanations for the observed transparency of p-type CuAlO_2 made to date, 1) the doping level is so low that, in thin-film form, the absorption is not strong enough to cause coloration or 2) that strong Cu-O hybridization significantly alters the optical excitations due to hole doping in CuAlO_2 compared to electron doping into WO_3 .

We believe that criteria such as the above may help establish potentially new TCO materials that may be made either in thin-film form or in bulk samples. They do not, of course, provide any guidance on whether or not the materials will have improved electro-optical properties. Next, we shall consider the use of bulk-phase diagrams, which also appears to have considerable promise in identifying novel TCOs.

We may expect future TCOs to be relatively complex structures with several cations and completely new phases. A good example of the search for novel materials is provided by the group from Northwestern University [26] which has performed a systematic investigation of oxide-phase space bounded by the known TCO species—In, Zn, Sn, Cd, and Ga. The search has followed the guidelines discovered above. The novel TCO phases discovered to date suggest possibilities for enhanced mobility materials. Firstly, 2-dimensional layered structures such as the homologous series of $\text{In}_2\text{O}_3(\text{ZnO})_k$ ($k = 1, 2, 3, 4, 5, 7, 11$) phases (27) suggest the possibility of preferential doping on “spacer” layers, with carrier injection into unperturbed conduction layers. Moriga [28], commented that the $k = 1$, and $k = 2$ members may only be stabilized by partial substitution of Ga for In. Secondly, co-substitution may be an effective means of altering TCO properties. This could lead to enhanced mobility along the conduction layers because they are otherwise undoped, and therefore, free of ionized impurity scattering

The extensive 40 at. % co-substitution of $\text{Zn}^{2+}/\text{Sn}^{4+}$ for two In^{3+} in In_2O_3 (versus only 6 at. % Sn substitution in ITO) results in excellent optical properties with only minor reductions in conductivity [29]. The analogous $\text{Cd}^{2+}/\text{Sn}^{4+}$ co-substituted in In_2O_3 is under investigation by the Northwestern University group. Two other strategies that have emerged from this work concern electron hybridization, i.e., crystal structures with more than one cation site. For example, the first true-ternary compound TCO to be reported, $\text{Ga}_3\text{In}_5\text{Sn}_2\text{O}_{16}$ [30] has three of the key cations as structural components, rather than as dopants. These have 4-fold, 6-fold, and 7-fold coordination environments. The ordering between the various sites is believed to be important in governing the electrical and optical properties of the TCO. Unpublished work by the Northwestern University group shows the existence of a spinel solid solution, $(1-x)\text{CdIn}_2\text{O}_4-x\text{Cd}_2\text{SnO}_4$, over the range $0 \leq x \leq 0.75$. Again, the distribution of cations between tetrahedral and octahedral sites is believed to play an important role in determining the TCO properties.

It ought to be stressed that most of these new TCO phases have yet to be deposited as high-quality thin films. The bulk resistivities are typically in the 10^{-3} – 10^{-2} Ω cm range; however, the above mentioned solid solution exhibits conductivities approaching 3×10^{-4} Ω cm, which is comparable with, or superior to, that of ITO made by the same solid-state reaction method. In general, the properties of thin films are superior to those of bulk materials. There are two other key differences between bulk and films. Often, the solubility limits can be greatly enhanced in films, e.g., ITO, that incorporates only ~6 at.% in bulk, but several times this in films, depending on deposition conditions. Secondly, phases that are unstable in bulk can be metastabilized as films. The spinel phase of Cd_2SnO_4 is a good example of this behavior because it exists as a film but not as a bulk material. Note that Cd_2SnO_4 corresponds to $x = 1$ in the solid solution mentioned above, which is only stable for values of $x < 0.75$. The potential for novel stable and metastable phases in the unexplored phase space of the In-Zn-Sn-Cd-Ga-O system is very considerable, in our opinion.

KEY RECOMMENDATIONS FOR BASIC RESEARCH

Rather than presenting a summary of the foregoing discussion, we shall simply itemize the key topics for basic research and development: these being issues that we believe must be addressed for the development of next-generation materials that will be crucial for more demanding applications. This is not intended to be an exhaustive list but rather one that makes specific reference to earlier discussions in this paper.

- Materials' science issues
 - use *ab initio* calculations and empirical models in the search new materials
 - use bulk phase diagrams to identify new phases in binary and ternary TCOs
 - explore the importance of metastability and crystallinity
 - explore more complex oxide mixtures
 - study compounds other than oxides for required optical and electrical properties
 - develop highly conducting (say, resistivity less than 10^{-2} Ω cm) p-type materials
 - use a wider range of characterization methods to analyze films and crystals
 - develop methods of deposition to give high rates and low substrate temperatures

- investigate the use of single crystal compounds and alloys to assist evaluation of intrinsic properties
- investigate new approaches to the synthesis of device-ready materials

- Investigate scattering mechanisms
 - develop methodologies with which to identify materials with prospectively good electro-optical properties
 - use transport measurements to determine predominant scattering mechanism and to probe the band structure of the semiconductors
 - establish the upper limit in mobility
 - investigate screening effects
 - model and minimize the effects of neutral impurities and compensation
 - investigate the role of dipole fields on scattering
 - evaluate the importance of grain boundaries and linear defects

- Investigate the role of impurities and defects
 - establish the role of oxygen vacancies
 - investigate co-doping of films and crystals
 - determine the importance of non-ionized impurities
 - learn how to increase ionization efficiency of impurities

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