Preface

Transparent Conducting Oxides (TCOs) are a unique class of materials that exhibit both transparency and electronic conductivity simultaneously. These materials have found wide spread use in displays, photovoltaics, low-e windows, and flexible electronics. In many of these applications, the TCO's, are enabling in their role as transparent contacts. However, increasingly, the demands required extend beyond the combination of conductivity and transparency, where indeed higher performance is needed, but now include work function, morphology, processing and patterning requirements, long term stability, lower cost and elemental abundance/green materials. As these needs have begun to emerge over the last 5 years they have stimulated a dramatic resurgence of research in the field leading to many new materials and processes. Overall it is the purpose of this book to provide both a snapshot of the new and enabling work in the field and to provide some indications of what might be coming next. We note that now the field of Transparent Conductors (TC's) includes not only conventional TCOs but also metal and carbon nano-composites, grapheme and polymer based TC materials. While the book primarily focuses on the TCOs some comparisons are made to the newer materials. To do this we have assembled a group of authors representing most of the leading groups in the field.

Historically, TCOs were limited primarily to tin oxide with fluorine doping, zinc oxide with aluminum doping and Indium tin oxide. Over the past 5–10 years the field has exploded to include a vastly increased number of n-type materials and to add in a class of new p-type materials. In addition, the historically held view that crystalline materials have superior properties, has been challenged by an emergence of new amorphous TCOs that have properties as good as or better than their crystalline counterparts. These materials have led to the development of amorphous oxide transistors which offer the advantage of low temperature processing and the promise of flexible electronics on polymer substrates. In their role as a channel material in thin film transistor structures, TCO's with controlled carrier densities are often termed transparent oxide semiconductors (TOS) since their key properties

may lie in the limited to non-conductive regime. To capture this diversity of materials, processing and applications, we have organized the book as follows.

Chapter 1 introduces TCOs and covers the historic materials and their properties and uses this background to put some of the newly emergent materials into a technological context. *Chapter 2* presents a detailed discussion of the basic electronic structures of TCO materials emphasizing the key properties which give them their unique properties. *Chapter 3* then provides an overview of methods for the measurement and interpretation of transport properties in TCOs based of the Drude model with a focus on the method of four coefficients for the determination of critical parameters such as carrier type, mobility and scattering mechanisms in multinary oxides. *Chapter 4* covers the basic physics of, and practical tools for, the characterization of important TCO parameters including atomic structure, optical properties, electrical transport, work function and other properties that must be better understood as TCO's become used in novel applications such as thin film transistors. *Chapter 5* presents a picture of the current In based TCOs covering both the traditional $InSnO_x$ materials which have been the gold standard of TCOs and the emerging amorphous materials. *Chapter 6* presents an overview of the tin oxide based TCO materials. While historically these materials have been produced in exceptionally large areas new work has begun to improve their properties. *Chapter 7* reviews the state of the art for ZnO. This material, due to its natural abundance and the ease with which it can be deposited via both physical and chemical routes, has important applications both as a traditional transparent contact and great potential as an active optoelectronic material. To realize this potential, a great deal of work has been done to identify new approaches to both n and p-type doping. *Chapter 8* looks at the rapidly expanding class of multi-cation TCO materials. Recent work shows that much higher performance can be achieved in some TCO materials by the addition of elements that serve to modify defect and electronic band structure. This ability to create multi-component TCO materials without significantly degrading key transport parameters (e.g., carrier mobility) is a characteristic of the TCO class of materials. *Chapter 9* looks at the theoretical framework used to describe the band structures of both n- and p-type oxide materials and includes a discussion of emerging non-oxide based transparent conductors. This fundamental background provides the basis for a discussion on considerations for the discovery of new high performance transparent conducting materials. *Chapter 10* considers new materials that have emerged in the transparent conductor field over the last few years. Historically, the set of elements whose oxides provide useful TCO properties have been constrained to single or mixed oxides of In, Ga, Zn, Sn, and Cd. This chapter discusses how the pallet of useful elements for TCO applications has grown to open whole new classes of materials.

The second half of the book begins to address the applications of TCOs and how new materials can significantly change the paradigm for a technology or be enabling for another. *Chapter 11* discusses the application of TCO materials for solar energy and energy efficiency applications. In fact, though a key focus is the active devices like PV, the reality is that in terms of energy efficiency, the use of TCO's in energy conservation applications are greater in the near term than

production. In any case it needs to be looked in an integrated way which is the theme of the chapter. *Chapter 12* considers the idea that TCOs need not be planar films but that in many cases the films can be enabling or integrated into a more complex hybrid (organic/inorganic for example) device by having a nanostructured morphology. Enabling this is a broad set of solution and PVD approaches to creating controlled nanostructures in TCO materials from texture to nano-rods etc. *Chapter 13* explores the application of amorphous TCOs and their semiconducting/insulating TOS counterparts to develop new flexible and transparent electronics for displays and more. The demonstration of TOS materials as a channel materials in thin film transistor applications has dramatically altered the potential for amorphous oxides in an increasingly diverse set of technologies. *Chapter 14* considers the potential for making true oxide based p/n junctions to realize active devices that are entirely based on TCO/TOS materials. The ability to make such junctions expands the potential for oxide based electronics including transparent electronics, oxide based solar cells and LED/lasers. Finally, *Chap. 15* discusses the scaling of TCO materials to large area industrial processing. This is a key issue as it addresses some of the critical properties dependence on process parameters.

We note that there is increasing interest in solution processed transparent conductors consisting of nanostructures of carbon (nanotubes), oxides (nanorods i.e., ZnO) and metals (such as Ag nanorods). However, thus far although they are very interesting, these materials still have conductivities approximately an order of magnitude below those for high performance TCOs. Over the next few years we expect these materials will become increasingly important perhaps in combination with TCO materials. Their inclusion in this volume at present is, however, beyond the intended scope of this publication.

This book presents a picture of an important class of materials that has, in recent years, drawn increasing interest for applications in active devices and as a critical component in any structure that requires both electrical connectivity and optical transparency. Despite their technological importance and relatively long history of use, our understanding of the existing set of TCO materials are only now receiving the kind of combined fundamental/experimental materials research attention that will inevitably lead to new materials discoveries and novel applications. Overall, it is clear that transparent conductive oxides and transparent conductors are a vibrant field that is advancing rapidly across an ever broadening spectrum of applications.

We hope this book will provide a valuable reference for those interested in the topic and stimulate additional development of new TCO materials and their applications.

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