# Preface

This essential reference provides the most comprehensive presentation of the state of the art in the field of solar photovoltaics (PV). This growing field of research and applications is currently being supported by numerous governmental, industrial, and educational initiatives in the United States, Asia, and Europe to overcome solar grid parity. The technology is particularly intended for increasing the usage of renewable energy resources for energy production. The next-generation solar PV is focused on improving the single junction cell conversion efficiency to near the Shockley-Queisser limit and also working toward reducing the gap between cell and module efficiencies while reducing the cost of the present process lines for existing flexible PV. This book can be used as a research and professional reference for teaching earth-abundant and inorganic-organic hybrid solar photovoltaics. World-renowned authors explore the topic in nine engaging chapters: (1) 3D Geometries: Enabling Optimization Toward the Inherent Limits of Thin-Film Photovoltaics; (2) Earth-Abundant $Cu_2ZnSn(S,Se)_4$ (CZTSSe) Solar Cells; (3) $Cu_2ZnSnS_4$, $Cu_2ZnSnSe_4$ and Related Materials; (4) ZnO Doping and Defect Engineering—A Review; (5) Hydrogen Production and Photodegradation at $TiO_2$/Metal/CdS Sandwich Using UV-Visible Light; (6) Organic Photovoltaics; (7) Nanophase Engineering of Organic Semiconductor-Based Solar Cells; (8) Solar Cell Characterization; and (9) Applications.

The first article by Debnath et al. provides an overview and outlook of 3D geometries with the promise of improved efficiency. A number of 3D nano and microscale approaches based on silicon (Si), cadmium telluride (CdTe), copper indium sulfide (CIS), copper indium gallium selenide (CIGS), gallium arsenide (GaAs), and Zinc oxide (ZnO) absorbers are discussed. The approaches attempt to decouple conflicting criteria for optimization of performance, eliminate particular criteria, modify materials properties, or achieve some combination thereof. Significant challenges do exist for scaling-up the current designs based on nano and micro-manufacturing. Research on 3D geometries for light management are also presented, as are developments of back contacts. A number of third-generation 3D PV devices are approaching double digit efficiencies, and there is a significant crosstalk between planar and 3D solar cell developments.

The main challenge in solar PV technology is to reduce the cost and use earth-abundant elements for manufacturing reliable, efficient PV devices for global clean energy needs. A promising pathway to reduce PV cost is the use of thin-film technologies in which thin layers of earth-abundant photoactive materials are deposited on large-area substrates. One of the most promising thin-film PV technologies is based on earth-abundant copper-zinc-tin-chalcogenide-based kesterites, $Cu_2ZnSnS_4$ (CZTS), $Cu_2ZnSnSe_4$ (CZTS(Se)). These materials are presented in great detail in the next two contributions. Significant developments have been made on CZTS(Se) devices in the past few years, reporting $\sim$11 %-efficient solar cell. However, CZTS(Se) PV technology is currently in its amateur state and requires extensive research to become marketable in the near future. The chapter by Das et al. covered a limited overview of the technologies employed to prepare CZTS-based materials. CZTS absorbers have been prepared by a variety of physical vapor deposition techniques such as evaporation, sputtering, and pulsed laser deposition. In addition, they have been prepared by a variety of nonvacuum deposition techniques such as solution processing, nanocrystal-based deposition, electrodeposition, screen printing, spray pyrolysis, and chemical bath deposition. CZTS thin-film technologies can be deposited on a wide variety of substrate materials making it possible to manufacture very lightweight, flexible solar cells on metals, sodalime glass, and plastic substrates, and thus have correspondingly lower cost. This CZTS has a direct bandgap of 1.4–1.5 eV and high optical absorption coefficient for photon energies higher than the bandgap such that only a few microns of material are needed to absorb most of the incident light, and hence material and production costs are reduced. Thin-film CZTS solar cells can be 100 times thinner than silicon-wafer cells. The CZTS cells consist of at least five layers: (i) substrate (soda-lime glass); (ii) back contact (Mo); (iii) CZTS absorber; (iv) CdS emitter; and (v) front contact (ZnO, ITO).

The article by Shiyou Chen introduces the fundamental material properties of CZTS, CZTS(Se), and related quaternary compound semiconductors, including how they are derived from binary II–VI semiconductors, crystal structures, electronic structure, alloys, thermodynamic stability, secondary phases, defects, and surfaces. Their influence on electrical, optical, and photovoltaic performance is discussed. As a result of the increased chemical and structural freedom of these quaternary semiconductors, these properties are much more flexible and complicated than those of simple elemental and binary semiconductors, and are also critical for understanding the limiting mechanism to the solar cell performance. Detailed band structure calculations for CZTS-related materials are also reported. Growth and fundamental understanding of the photoactive CZTS layers with reduced defect density, compositional variations, grain boundary doping, and microstructure and their correlation with photovoltaic properties are necessary to increase the cell efficiency further.

The current status of ZnO n-type and p-type doping is comprehensively reviewed in the chapter by Xiu and Xu, including the different doping methods and dopant sources. ZnO is inexpensive, nontoxic, and compatible with semiconductor manufacturing processes. Also, ZnO has been synthesized with a variety of nanostructures. The nanoscale p–n junctions can increase the injection rate of carriers many times more than that for a planar ZnO diode. Based on these advantages, ZnO has seen a surge of research interest aimed at achieving high efficiency for ultrabright LEDs, laser diodes, and ultrafast photodetectors. However, the main obstacle hindering ZnO application is a reliable method for fabricating p-type ZnO material with a high hole concentration, high mobility, and low resistivity. The current state of p-type doping of ZnO seems to be similar to that of p-type doping of GaN more than 20 years ago. Therefore, it is believed that, with continuing innovation, the p-doping difficulty in ZnO could be solved in the near future.

As clean energy resources, sunlight and water are abundant and universally available, and hence there is immense interest for energy applications. Hydrogen production utilizing sunlight and water is a sustainable and logical approach for constant energy generation. This is an example of a conversion of solar energy into chemical energy. As a well-known photocatalyst, $TiO_2$ is of interest and has been examined persistently for water splitting for a range of reasons, including its wide-ranging pH stability, nontoxicity, and good photoactivity in the presence of UV light. The chapter by Manivannan et al. discusses a wet chemical approach to synthesize anatase-only $TiO_2$, incorporate platinum group metals (PGMs), and subsequently deposit a chalcogenide to form a unique high surface area nano-composite. Optical, microstructural, and photoelectrochemical studies have shown that the as-prepared $TiO_2$ has a particle size of 20 nm, demonstrates 60 % higher surface area compared to the commercial $TiO_2$, and exhibits superior photoelectrochemical responses (e.g., 60 % increase in photocurrent) indicating that it is a promising base material for preparing visible light active composites. Among the three PGMs studied for photocatalytic hydrogen generation, $\sim$0.79 wt% of Pt on as-synthesized $TiO_2$ is noted to be most useful: attributable at least in part to its known stability relative to other PGMs during photocatalysis. To conclude, metal oxides such as $TiO_2$ can be used as a replacement for polysulfide stabilizers with the dual benefit of its photodegradation as well as hydrogen generation.

The contribution by Delongchamp provides details about the origin of organic photovolatics (OPV) and the future outlook of these solar cell devices. The active layer of an OPV solar cell is composed of hydrocarbon-based organic materials. OPV occupies a special niche among solar energy technologies in that it could potentially satisfy the growing energy needs of the world with a product that is sustainable, elementally abundant, and cheaply manufactured. OPV cells have recently seen a dramatic uptick in reported efficiencies, with power conversion efficiencies reaching $\approx$11 %. These increases in power conversion efficiency have largely been driven by the development and discovery of new OPV active layer materials and new ways to process them. The technology has gained significant commercial attention over the past decade, as its unique attributes merit consideration for a place in the landscape of distributed energy generation devices. Some of OPV's advantages include a flexible form factor and facile processing, either from fluids or from vacuum deposition.

The chapter by Yang et al. describes chemical synthesis approaches to tune the electronic energy levels in low bandgap polymers to match the energy levels of fullerene derivative acceptors for optimized charge transfer. They also review recent progress in tuning the film morphologies with solvent annealing, thermal annealing, processing additives, and compatibilizers. The development of OPVs toward future commercialization is still underway. Very recently, the organometal halide perovskite solar cells have shown great promise with efficiency of over 15 %. The remarkable success of organic–inorganic hybrid perovskites is based on the combination of the advantages of organic materials, such as low cost, solution processing capability, and flexibility, with the advantages of inorganic semiconductors, such as high crystallinity and excellent charge transport properties.

The solar cell characterizations covered in the chapter by Hamadani and Dougherty address the electrical power generating capabilities of the cell. Some of these covered characteristics pertain to the workings within the cell structure (e.g., charge carrier lifetimes) while the majority of the highlighted characteristics help establish the macro performance of the finished solar cell (e.g., spectral response, maximum power output). Specific performance characteristics of solar cells are summarized in this article, while the method(s) and equipment used for measuring these characteristics are also emphasized.

Lastly, the various solar cell applications are reviewed in the chapter by Chen et al. The important applications in space are discussed first, including the history, development, and materials consideration of solar panels in space. Among terrestrial applications, the most widely used is solar power generation for grid utilities. Building-integrated photovoltaics (BIPV) have been identified as a fast growth application with a large market, and the latest developments in hybrid solar, transparent solar panel are discussed. In addition, solar cells have also been used in automotives, public electric facilities, such as road lighting, water pumps, vending machines, and various consumer electronics such as watches and hand calculators. The solar cell efficiency, life cycle, and cost of these various applications are reviewed. Finally, this chapter provides an overview of the latest solar panel technology and the major solar panel manufacturers worldwide, as well as a broad look at the current solar market and the outlook for the future.

Overall, the nine chapters in this book provide the reader an excellent resource for understanding materials for solar photovoltaics over a wide range of topical areas.

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