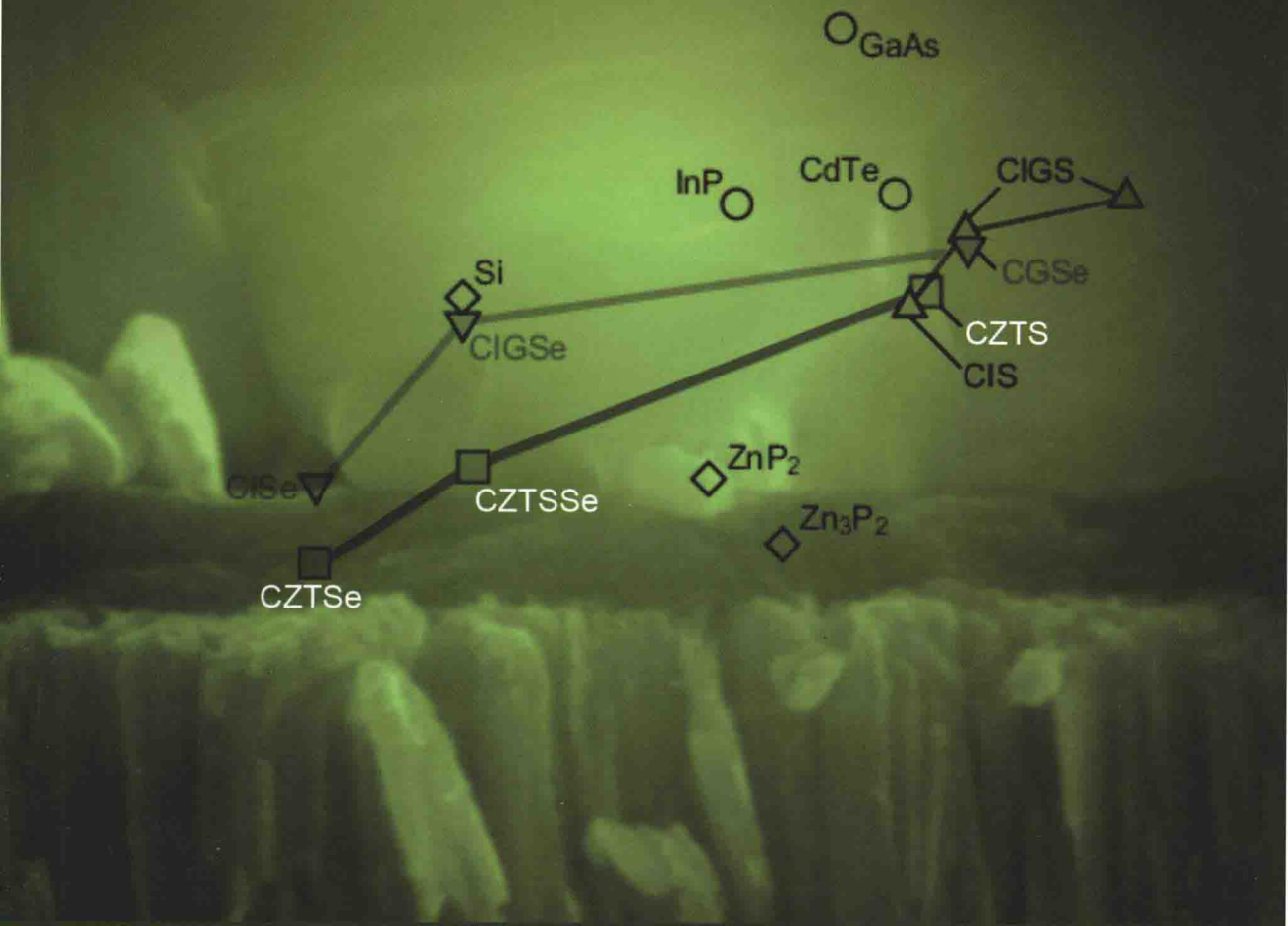
Copper Zinc Tin Sulfide-Based Thin Film Solar Cells

Edited by **Kentaro Ito**



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Edited by

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Preface

The most cost-effective route to solar cell fabrication was unlocked by utilizing thin-film technology. The first research papers on this type of cell date back to the 1960s. The semiconductor thin film consisting of a II-VI or I-III-VI_2 compound is normally used in the solar cell as an optical absorber with the thickness of microns. It is prepared on a low-cost substrate such as a glass plate, a metal sheet, or a plastic sheet. It was found in the late 1980s that the thin film of quaternary compound Cu_2ZnSnS_4 also has a suitable energy band and exhibits a photovoltaic effect. In this book we deal with the multinary compound semiconductors which belong to the tetragonal crystal system and have the optimal band gap for photovoltaics: the quaternary sulfide, its alloy, and a selenide. The chemical formulae of the latter are represented as $Cu_2ZnSn(S_xSe_{1-x})_4$ and $Cu_2ZnSnSe_4$. The purpose of this book is to describe current development of thin-film solar cells, from the viewpoint of device performance and absorber processing. We also describe the physical and chemical properties of these compounds, which are considered to play an important role in determining the efficiency of the solar cells.

In the mid-1970s, Professor A. G. Milnes of Carnegie Institute of Technology visited our University in Nagano to speak on the subject of solar cells. At that time he was a visiting scholar at the Tokyo Institute of Technology. He stressed the importance of cost in producing solar cells, and predicted that photovoltaics would not be of any practical use if the cost was higher than the threshold value (equal to ten cents per watt). He made numerous references to this threshold in his talk. He was interested in developing a low-cost GaAs solar cell which is grown epitaxially on a mono-crystalline substrate, a substrate which could be made reusable by detaching it many times from the epitaxial layer using selective chemical etching. Around that time, the efficiency of a GaAs solar cell was 22% while that of a CdTe thin-film solar cell was 8%. Although his concept is indirectly connected to the recent development of a GaAs solar cell, the efficiency of which has approximately reached the theoretical upper limit, it has not been applied to low-cost solar cells because the large-area mono-crystals are not available. By taking account of the rise in electricity rates (Consumer Price Index) during the past four decades, his threshold has to be upgraded to 45 (54) cents per watt at present. It is interesting to note that this converted threshold is only 1.5 times lower than the price of CdTe thin-film solar modules in 2013, as shown in Chapter 2. Despite polycrystalline nature, cost-effective performances of thin-film solar cells are preferable to those of mono-crystalline solar cells.

Multinary compound semiconductors have an absorption coefficient $>10^4\,cm^{-1}$ due to the direct nature of the band gap. Films of thickness 1 μm can absorb almost all the photons in the solar spectrum of wavelength shorter than near-infrared wavelengths, and operate as efficient photocurrent suppliers. The direct band gap is within an optimal range for solar cells, that is, 1.0–1.5 eV. The theoretical upper limit of efficiency for the solar cells is estimated to be 32–34%. There is still room for improvement in the present cell performance

via a high-quality absorber layer and the optimization of device structure. Since all the chemical elements of the compound are Earth-abundant, the material cost of the absorber can be much lowered in comparison to the II-VI or I-III-VI_2 thin-film solar modules in which the absorbers are composed of rare elements such as Te and In.

For the sake of simplicity, the chemical formulae are often abbreviated by replacing copper, zinc, tin, sulfur, and selenium with C, Z, T, S, and Se, respectively, and the suffixes are omitted. Photovoltaic devices which consist of these compounds are referred to as CZTS-based thin-film solar cells.

In the first chapter of Part I it is described how the concept for CZTS-based thin-film solar cells is derived from the physical principle of photovoltaics and also from the viewpoint of abundant natural resources. In the second chapter, their prospects are discussed by reviewing recent advances in producing thin-film solar modules, among which CdTe modules exhibit a learning curve pointing at price $US 0.7 per peak watt.

In the first chapter of Part II, it is described that the principal structure type of CZTS is kesterite, and the existence of some antisite point defects in the compound is demonstrated by neutron diffraction. Relatively small electron mass and high optical efficiency of the multinary compounds are deduced from theoretical studies of the energy band structure and complex dielectric function, respectively. We learn how CZTS is in thermal equilibrium with volatile sulfur and tin sulfide at growth temperatures, and that the existence of secondary phases in CZTS should be identified using specific analyses. Bulk CZTS single crystals are grown by solution growth, and their transport property is evaluated by Hall measurements. Physical properties of Cu_2-II-IV-VI_4 compounds are systematically compiled such that their data can provide useful information for the design of thin-film solar cells.

Various processes involved in the preparation of high-quality absorbers for solar cells are introduced in Part III. Study of thin-film CZTS solar cells reveals that a Cu-poor and Zn-rich absorber – prepared by sulfurizing a precursor – is required for the improvement of cell efficiency. Disordered CZTS thin films are first sputter-deposited from metal targets in a residual vapor pressure of H_2S and are then annealed in sulfur vapor. After coevaporation techniques are elucidated to grow thin-film compounds, their application to CZTS-based thin-film solar cells are reviewed. CZTSe thin films are prepared by annealing the precursor in Se vapor, which is formed by coating a substrate with the ink composed of CZTS nanocrystals. CZTS thin films are prepared by oxidation and subsequent sulfurization of an oxyhydrate precursor which is coated by the sol-gel method. Mono-grain crystallites of the CZTS-based compounds are grown by a flux method and they are arranged in a mono-grain layer to make solar cells.

Part IV is on the device physics of thin-film solar cells. According to the microscopic observation by SKPM and conductive AFM, the enhanced minority carrier collection takes place at the grain boundaries of multinary compounds. The efficiency of CZTS-based thin-film solar cells fabricated by coevaporation and annealing is at least partly correlated with the defect density in the absorber. The device characteristics of the thin-film solar cells are reviewed, and the high series resistance in them is considered attributable to such a secondary phase as ZnSe. Using the hydrazine pure-solution approach, a CZTSSe thin-film solar cell with 12.6% efficiency is obtained. The possible effect of band tailing on the open-circuit voltage is discussed.

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Part I
Introduction

1

An Overview of CZTS-Based Thin-Film Solar Cells

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1.1 Introduction

This book deals with the thin-film solar cell with optical absorber layer composed of the copper-zinc-tin-sulphide-based quaternary semiconductor represented by chemical formula Cu_2ZnSnS_4 or related compound semiconductors. Throughout this book, we abbreviate the quaternary compound as CZTS. The concept of CZTS thin-film solar cells is based on the following principles. The compound semiconductor meets two necessary conditions for efficient solar cells. One is the direct nature of the band gap and the other is its width within a certain optimal range for photovoltaic cells. Because the pre-factor of absorption coefficient for the CZTS thin film is large enough the layer of just micron thickness is able to absorb sunlight sufficiently, and the use of it as an absorber does not have any damaging effects on photocurrents. The probability of radiative recombination in the film is able to exceed that of non-radiative recombination if both absorption and emission of photons are caused by an allowed direct transition of carriers between valence and conduction bands without any intermediaries such as crystal defects and phonons. It is therefore possible for cell efficiency to approach the theoretical limit if Shockley–Read–Hall-type recombination centers, which play a role in bypassing the direct recombination, are diminished and at the same time a device structure to confine excited electrons in the CZTS base layer is implemented. The CZTS semiconductor is potential candidate material for terawatt (TW) -scale

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photovoltaic energy conversion: a fractional amount of the elemental constituents produced annually is sufficient to fabricate CZTS thin-film solar cells which can supply renewable energy on a scale comparable to the world's electricity consumption. The multiplicity of the compound is advantageous in designing the semiconductor material for photovoltaic devices, because we can control its physical properties depending on a substitution of the cation or anion included in the fundamental tetrahedron for another cation or anion and we can also avoid the undesirable use of rare or toxic elements. The incomplete (9%) substitution of sulfur for selenium is a typical example, which has lead to the achievement of alloy thin-film solar cells with over 10% efficiency [1, 2].

The physics of the photovoltaic effect are described in Section 1.2, including: the spectral irradiance of solar radiation and the influence of the Earth's atmosphere on it; the upper limit of conversion efficiency of a single-junction solar cell which is evaluated on the basis of a detailed balance model; an optimal range of energy band gaps for photovoltaic energy conversion; optical absorption in semiconductor thin films and the estimation of the thickness of the absorber layer required for an efficient thin-film solar cell; and important roles of semiconductor pn-(positive or negative) homo- and hetero-junctions in the photovoltaic effect. In Section 1.3 we describe the pursuit of an optimal semiconductor for photovoltaic applications which have a band gap within the optimal range. The history of the thin-film solar cell is first discussed, including studies on some mono-crystalline semiconductor materials and their photovoltaic applications and the development of a chalcopyrite-type thin-film solar cell for comparison. We then describe how the concept of CZTS technology originated. Finally, we describe our synthesis and characterization of the CZTS absorber and n-type buffer layers to conclude the chapter.

1.2 The Photovoltaic Effect

1.2.1 Solar Radiation

1.2.1.1 Extra-terrestrial Radiation

At the core of the Sun, nuclear fusion of hydrogen releases massive heat. The Sun is surrounded by a thin atmosphere which consists mostly of hydrogen atoms. This is the so-called photosphere that absorbs the heat and emits electromagnetic radiation into outer space with almost the same spectral radiation as that of a black body in thermal equilibrium at a high temperature T_S. According to Planck's formula, the power emitted per unit projected area of the black body into a unit solid angle per unit frequency interval is given by the spectral irradiance $L_\nu(T_S)$, defined

$$L_\nu(T_S) = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu / k_B T_S) - 1} \tag{1.1}$$

where ν is the frequency of radiation, c is the light speed, h is the Plank constant, and k_B is the Boltzmann constant. The photon energy of electromagnetic oscillation at frequency ν is given by $h\nu$. The solid angle Ω_S of the Sun (in steradians) which is seen from the Earth is calculated as:

$$\Omega_S = \frac{\pi r^2}{R^2} = 6.79 \times 10^{-5} \tag{1.2}$$

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