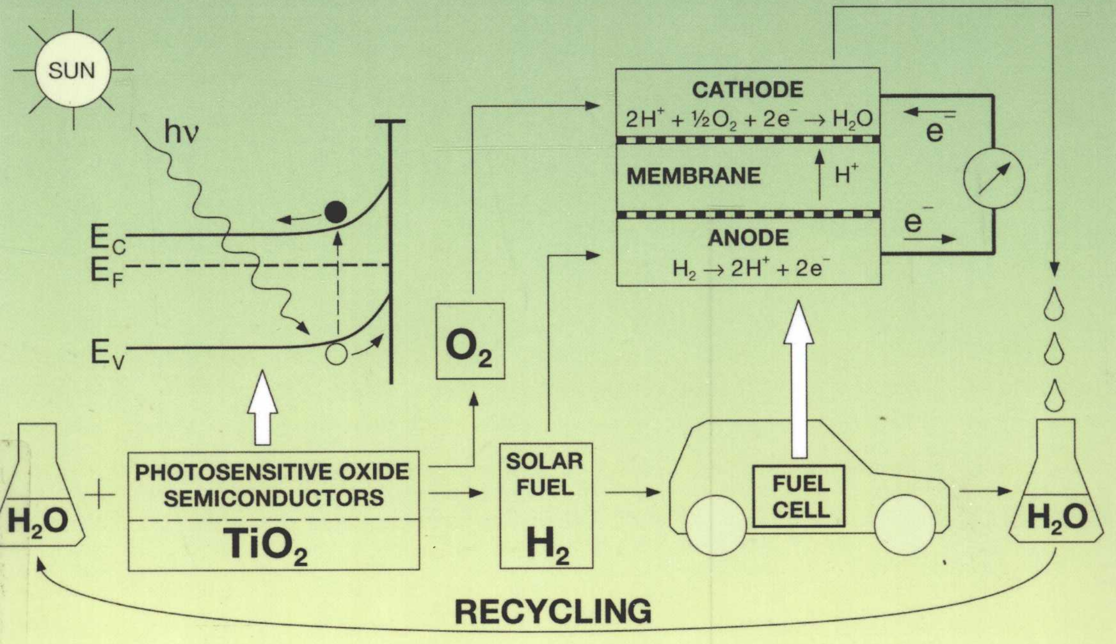
Oxide Semiconductors for Solar Energy Conversion

Titanium Dioxide



Janusz Nowotny

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Titanium Dioxide

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Oxide Semiconductors for Solar Energy Conversion: Titanium Dioxide
Janusz Nowotny

I dedicate this book to Professor Adam Bielański,
prominent chemist, outstanding educator,
and a man of exceptional integrity, on
the occasion of his 99th birthday.

Janusz Nowotny

Series Preface

The subjects and disciplines of chemistry and chemical engineering have encountered a new landmark in the way of thinking about developing and designing chemical products and processes. This revolutionary philosophy, termed *green chemistry and chemical engineering*, focuses on the designs of products and processes that are conducive to reducing or eliminating the use and/or generation of hazardous substances. In dealing with hazardous or potentially hazardous substances, there may be some overlaps and interrelationships between environmental chemistry and green chemistry. Whereas environmental chemistry is the chemistry of the natural environment and the pollutant chemicals in nature, green chemistry proactively aims to reduce and prevent pollution at its very source. In essence, the philosophies of green chemistry and chemical engineering tend to focus more on industrial application and practice rather than academic principles and phenomenological science. However, as both a chemistry and chemical engineering philosophy, green chemistry and chemical engineering derive from and build on organic chemistry, inorganic chemistry, polymer chemistry, fuel chemistry, biochemistry, analytical chemistry, physical chemistry, environmental chemistry, thermodynamics, chemical reaction engineering, transport phenomena, chemical process design, separation technology, automatic process control, and more. In short, green chemistry and chemical engineering are the rigorous use of chemistry and chemical engineering for pollution prevention and environmental protection.

The Pollution Prevention Act of 1990 in the United States established a national policy to prevent or reduce pollution at its source whenever feasible. And adhering to the spirit of this policy, the Environmental Protection Agency (EPA) launched its Green Chemistry Program in order to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products. Global efforts in green chemistry and chemical engineering have recently gained a substantial amount of support from the international communities of science, engineering, academia, industry, and government in all phases and aspects.

Some of the successful examples and key technological developments include the use of supercritical carbon dioxide as a green solvent in separation technologies; application of supercritical water oxidation for destruction of harmful substances; process integration with carbon dioxide sequestration steps; solvent-free synthesis of chemicals and polymeric materials; exploitation of biologically degradable materials; use of aqueous hydrogen peroxide for efficient oxidation; development of hydrogen proton exchange membrane (PEM) fuel cells for a variety of power generation needs; advanced biofuel productions; devulcanization of spent tire rubber; avoidance of the use of chemicals and processes causing generation of volatile organic compounds (VOCs); replacement of traditional petrochemical processes by microorganism-based bioengineering processes; replacement of chlorofluorocarbons (CFCs) with nonhazardous alternatives; advances in design of energy-efficient processes;

use of clean, alternative, and renewable energy sources in manufacturing; and much more. This list, even though it is only a partial compilation, is undoubtedly growing exponentially.

This book series on Green Chemistry and Chemical Engineering by CRC Press/ Taylor & Francis is designed to meet the new challenges of the twenty-first century in the chemistry and chemical engineering disciplines by publishing books and monographs based on cutting-edge research and development to the effect of reducing adverse impacts on the environment by chemical enterprise. In achieving this, the series will detail the development of alternative sustainable technologies that will minimize the hazard and maximize the efficiency of any chemical choice. The series aims at delivering the readers in academia and industry with an authoritative information source in the field of green chemistry and chemical engineering. The publisher and its series editor are fully aware of the rapidly evolving nature of the subject and its long-lasting impact on the quality of human life in both the present and future. As such, the team is committed to making this series the most comprehensive and accurate literary source in the field of green chemistry and chemical engineering.

Sunggyu Lee

Foreword

Interest in using solar energy in the production of environmentally friendly fuel is increasing. The research focuses on the generation of hydrogen by solar water splitting. To address this challenge, we need a new generation of materials that are reactive within both light and water and, at the same time, are resistant to corrosion and photocorrosion in water. Oxide semiconductors are expected to meet these requirements. This book by Prof. Nowotny is addressing the increasingly urgent need for a treatise on oxide semiconductors in general and TiO_2-based semiconductors in particular.

Titanium dioxide is an emerging material for a wide range of energy-conversion applications, including photocatalysts for solar water purification, photoelectrodes for the generation of hydrogen fuel, photovoltaic solar cells, chemical gas sensors, as well as alternative environmentally friendly applications. This is the reason why there has been an accumulation of reports on titanium dioxide. This book, which is the first treatise on TiO_2, will be of a great help to the research community involved in the studies on the properties of this oxide material.

At present, the reported experimental data on TiO_2 are not compatible even for the same systems. The studies, frequently based on the trial-and-error strategy, do not lead to well-defined and reproducible properties. The lack of compatibility does not allow derivation of a general theory on the photocatalytic performance of TiO_2. This book indicates that the problem of compatibility may be addressed using defect chemistry as a framework in the processing of TiO_2-based photocatalytic systems, and shows that the application-related properties of oxide crystals are closely related to lattice imperfections (point defects). Consequently, defect engineering should be applied in the formation of oxide semiconductors for the modern-day technology.

The book of Prof. Nowotny is expected to serve as a handbook for the large research community in the areas of photocatalysis, solid state science, electrochemistry, and materials science and engineering.

Professor Sebastian Fiechter
Institute for Solar Fuels
Helmholtz-Center Berlin for Materials and Energy
Berlin, Germany

Foreword

There is a large and growing interest in oxide semiconductors owing to their wide range of applications in electronics (capacitors, resistors, thermistors, piezoelectrics, high T_c semiconductors), sensors, and fuel cell electrodes. Moreover, the application of oxide semiconductors in photoelectrochemical and photovoltaic cells has the tremendous potential to address our future energy needs through an essentially unlimited energy resource, the Sun.

Oxide Semiconductors for Solar Energy Conversion: Titanium Dioxide describes the fundamental properties of oxide materials that make them so attractive for applications. Moreover, it becomes increasingly clear that the performance of oxides in a wide range of applications is related to point defects. This book provides a comprehensive survey of defect chemistry and defect-related properties of oxides, including electronic structure, charge transport, diffusion, and segregation.

Oxide Semiconductors for Solar Energy Conversion: Titanium Dioxide is focused on titanium dioxide and TiO_2-based semiconductors, which are expected to form a new generation of silicon-free solar materials. This work of Professor Nowotny's is probably the only survey on semiconducting and photocatalytic properties of TiO_2 at present, particularly with respect to inclusion of the importance of defect chemistry. The research of the author in this area has attracted the prestigious Sir William Grove Award of the International Association for Hydrogen Energy.

This book should be welcomed by the large research community interested in oxide semiconductors in general and TiO_2 in particular, as well as the growing community interested in photocatalysis.

Professor Eric D. Wachsman
University of Maryland Energy Research Center
University of Maryland

Preface

The demand for energy is rising. At the same time, the increasingly apparent effects of climate change dictate the need to abandon fossil fuels and use renewable energy instead.

Solar energy is the most attractive source of renewable energy available in abundance, and this has led to global efforts to develop solar technologies. The amount of global energy needs is only a small fraction of the solar energy provided by the Sun to the Earth. However, the implementation of new solar energy conversion devices requires the development of novel, less expensive solar materials that can make solar energy more competitive. Awareness is growing that oxide semiconductors have the capacity to replace silicon in the development of the next generation of solar cells. This book is an attempt to provide a brief survey of the basic properties of oxide semiconductors, in general, and titanium dioxide (TiO_2), in particular. The scope of this book is limited to binary metal oxides.

Awareness is growing that titanium dioxide, TiO_2, may soon become a strategic raw material for the development of TiO_2-based photosensitive semiconductors for harvesting solar energy for a wide range of environmentally friendly applications. The present recognition of the significance of titanium dioxide has led to increasing interest in its basic properties, in general, and performance-related properties in solar energy conversion, in particular. This interest indicates the need for a written resource in which the properties of TiO_2 and the related scientific background can be presented in a concentrated form. The present book is an attempt to address this need.

Titanium dioxide is commonly known as a pigment for sunscreen blocker and toothpaste. There has been an accumulation of reports indicating that TiO_2 may also have interesting electrical properties, including semiconducting, metallic, and insulating properties. These properties can be imposed in a controlled manner by manipulations with lattice imperfections.

The growing awareness of the importance of TiO_2 as an emerging solar energy material has resulted in increasing interest in the photocatalytic properties of this compound. The studies, which are focused mainly on the rutile phase, frequently fail to recognize that the rutile structure is strongly defective and that its properties are closely related to defect disorder. Therefore, one of the aims of this book is to provide a brief overview on defect-related properties of rutile, including semiconducting properties and photoreactivity.

Titanium dioxide, along with its solid solutions and composites, is the promising candidate for the conversion of solar energy into other types of energy, such as chemical energy and electrical energy. The TiO_2-based photosensitive semiconductors can be used for photoelectrochemical generation of solar hydrogen fuel by water splitting, photocatalytic water purification, and the generation of electricity. Alternative applications include chemical gas sensors, pigments, dielectrics as well as self-cleaning, antipollution, antireflection, and antiseptic coatings.

This book presents a brief outline on selected aspects of solid-state electrochemistry of binary metal oxides, in general, and TiO_2, in particular. The focus is on electrical properties, mass and charge transport, reactivity, as well as photo-induced effects and the related applied properties of TiO_2 and its solid solutions. The multidisciplinary character of the related research areas includes the concepts of solid-state science, surface chemistry, photoelectrochemistry, and catalysis.

This book concentrates on defect chemistry and defect-related properties with the aim to establish a correlation between defect disorder and functional properties, such as catalytic, photocatalytic, and semiconducting properties. This correlation led to the development of defect engineering of TiO_2, which can be used in the processing of TiO_2-based semiconductors with desired performance.

Special thanks are due to my coworker Tadeusz Bak who has provided enormous technical assistance and personal support to me during the production of this book. This help in sincerely appreciated. Thanks are also due to Sean Li for reviewing selected parts of this book as well as to Ian Plumb and Gavin Conibeer for extensive discussions on solar energy conversion. I benefited a lot from discussions with Graeme Murch and Michio Yamawaki on segregation and diffusion, Faruque Hossain on energy-related aspects of defects in rutile, Truls Norby on the reactivity of rutile with water, Suk-Joong Kang on interface phenomena during sintering, Lou Vance on nuclear analytic techniques, as well as Han-Ill Yoo on defect chemistry in ternary oxides.

The critical mass for a book like this has been developed over many years. In this regard I would like to acknowledge the extensive collaboration on a wide range of problems related to solid state electrochemistry with J. Bruce Wagner, Jr, Werner Weppner and Eric Wachsman. I was fortunate to collaborate with Akira Fujishima, Helmut Tributsch, Sebastian Fiechter, and Yasuro Ikuma on photoelectrochemistry; Charles Gleitzer and Mietek Rekas on semiconducting properties of oxides; Eliette and Fernand Moya, Kazimierz Kowalski, and Zbigniew Grzesik on grain boundary diffusion; Kathryn Prince, Andrzej Bernasik, and Armand Atanacio on surface chemistry; Serge Zhuiykov on chemical gas sensors, and Zbyszek Adamczyk on the transport across interfaces. I had a great opportunity to collaborate with Carl Wagner on surface electrochemistry of transition metal oxides.

I enjoyed being part of a large research program on catalysis on semiconductors that was carried out under the leadership of Adam Bielański (Jagiellonian University, Cracow). This provided me with an opportunity to work with Krystyna Dyrek, Jerzy Dereń, Jerzy Haber, Staszek Mrowec, Romek Dziembaj, Zosia Kluz, Jacek Ziolkowski, and Grzegorz Ròg on a wide range of problems related to oxide semiconductors.

Finally, I must mention the most recent intensive and seminal collaboration with Nikolaus Sucher on solar water disinfection. This collaboration, which aims at bringing together the concepts of solid-state science and the concepts of biological science in relation to microbial agents, has been a great scientific adventure for me.

Special thanks are due to Sandi Steep for her great and friendly help in the preparation of this book. I would also like to thank Allison Shatkin, CRC Press, for efficient cooperation during the processing of this volume.

I sincerely appreciate the courtesy of Enrico Geninazza, Steve Forrest, and Charlie Lee of Cristal Global for providing the specimens of TiO_2.

This book is dedicated to researchers in the area of solid-state chemistry, materials science, photocatalysis, solid-state electrochemistry, photoelectrochemistry, catalysis, as well as the entire research community interested in the wide range of aspects of titanium dioxide. The increasing accumulation of reports on TiO_2 photocatalysis indicates that this community is rapidly growing.

This book is also addressed to graduate and postgraduate students who have basic knowledge in solid-state science.

Each chapter is followed by a list of assignable problems, which may assist students to address specific questions.

Janusz Nowotny
Sydney, 2011

Notation*

a	Activity ($a = f_i c_i$)
a_o	Jump distance [m]
AES	Auger electron spectroscopy
$A_{n,p}$	Kinetic constant for electrons/holes
AM	Air mass
B	Magnetic field [T (tesla)]
c	Chemical concentration [molar ratio]
C	Capacitance [F (farad)]
CPD	Contact potential difference [V]
d	Thickness [m]
D	Diffusion coefficient [m^2s^{-1}]
D_d	Diffusion coefficient of defects [m^2s^{-1}]
D_{chem}	Chemical diffusion coefficient [m^2s^{-1}]
e	Elementary charge [1.602189×10^{-19} C]
e'	Quasifree electron
E_a	Activation energy [eV, J/mol]
E_F	Fermi level [eV]
$(E_F)_n^*$	Light-induced quasi-Fermi level associated with electrons [eV]
$(E_F)_p^*$	Light-induced quasi-Fermi level associated with electron holes [eV]
E_C	Energy of the bottom of conduction band [eV]
E_g	Band gap [eV]
E_{in}	Incoming energy [J, eV]
E_{out}	Outcoming energy [J, eV]
E_{loss}	Energy losses [J, eV]
E_V	Energy of the top of valence band [eV]
$E(H^+/H_2)$	Energy level of the redox couple H^+/H_2 [eV]
$E(O_2/H_2O)$	Energy level of the redox couple O_2/H_2O [eV]
E_σ	Activation energy of electrical conductivity [J/mol]
ECE	Energy conversion efficiency
EMF	Electromotive force [V]
EPR	Electron paramagnetic resonance
f	Activity coefficient
F	Faraday constant [9.64845627×10^4 $Cmol^{-1}$]
F	Electric field [V/m]
FBP	Flat band potential [V]
G	Thermodynamic potential [J/mol]
h	Planck's constant [6.626176×10^{-34} J s]
$h^\bullet$	Quasifree electron hole

* The Kröger–Vink notation is defined in Chapter 1 (Table 1.1).

H	Enthalpy [J/mol]
ΔH_{seg}	Enthalpy change associated with segregation [J/mol]
ΔH_f	Enthalpy associated with defects formation [J/mol]
ΔH_m	Enthalpy change associated with defects motion [J/mol]
ISS	Ion scattering spectroscopy
I_r	Incidents of solar irradiance [W/m^2]
J	Current density [A/m^2]
J	Light flux [lm (lumen)]
k	Kinetic constant
k_B	Boltzmann's constant [8.6167×10^{-5} eVK^{-1}; 1.3807×10^{-23} $JK^{-1}atom^{-1}$]
K	Equilibrium constant
l	Length [m]
L	Langmuir [L] (1 L corresponds to a gas exposure of 10^{-6} Torr during 1 s)
LEED	Low energy electron diffraction
LEIS	Low energy ion scattering
L_D	Screening depth (Debye length) [m]
m	Mass of electron [9.1094×10^{-31} kg]
m_n	Reciprocal of the $p(O_2)$ exponent related to the concentration of electrons
m_p	Reciprocal of the $p(O_2)$ exponent related to the concentration of electron holes
m_S	Reciprocal of the $p(O_2)$ exponent related to thermoelectric power
$m^*_{n,p}$	Effective mass of electron/hole [kg]
m_σ	Reciprocal of the $p(O_2)$ exponent of electrical conductivity
m_φ	Reciprocal of the $p(O_2)$ exponent of work function
n	Concentration of electrons [m^{-3}]
N_A	Avogadro's number [6.023×10^{23}]
n_d	Concentration of defects
N(E)	Distribution of particles with respect to energy [$s^{-1}m^{-2}eV^{-1}$]
N_n	Density of states in the conducting band [m^{-3}]
N_p	Density of states in the valence band [m^{-3}]
p	Concentration of electron holes [m^{-3}]
$p(O_2)$	Oxygen activity [Pa]
PEC	Photoelectrochemical cell
R	Universal gas constant [8.3144 J mol^{-1} K^{-1}]
R	Resistance [Ω]
s	Surface area [m^2]
S*	Entropy [J $mol^{-1}K^{-1}$]
S_c	Configuration entropy [J $mol^{-1}K^{-1}$]
S	Thermoelectric power [V/K]
$S_{n,p}$	Thermoelectric power component related to electrons/holes [V/K]
S_v	Configuration entropy [J $mol^{-1}K^{-1}$]
SEM	Scanning electron microscope

SIMS	Secondary ion mass spectrometry
SPS	Surface photovoltage spectroscopy
STM	Scanning transmission microscope
$t_{n,p,i}$	Transference number of electrons/holes/ions
T	Absolute temperature [K]
TD	Thermal desorption
TPD	Thermally programmed desorption
TiO_2-PC	Polycrystalline TiO_2
TiO_2-SC	Single crystal TiO_2
TPB	Three phase boundary
UPS	Ultraviolet photoelectron spectroscopy
V_{bias}	Bias voltage [V]
WF	Work function [eV]
z	Number of electrons
Z	Impedance [Ω]
x	Distance [m]
XPS	X-ray photoelectron spectroscopy
α	Geometrical factor
β	Temperature coefficient of the band gap [eV/K]
ε	Dielectric constant
ε_o	Vacuum dielectric constant
γ	Surface tension [N/m]
Γ	Excess concentration [molar ratio]
η	Electrochemical potential [J/mol]
η_c	Total energy conversion efficiency
η_{QE}	Quantum energy conversion efficiency
Θ	Surface coverage [ratio]
μ	Chemical potential [J/mol]
μ_n	Mobility of electrons [$m^2V^{-1}s^{-1}$]
μ_p	Mobility of electron holes [$m^2V^{-1}s^{-1}$]
μ_i	Mobility of ions [$m^2V^{-1}s^{-1}$]
σ	Electrical conductivity [$\Omega^{-1}m^{-1}$]
v	Frequency [Hz (hertz)]
$\rho(x)$	Charge distribution (linear) [Cm^{-1}]
ρ	Resistivity [Ωm]
ψ	Electrical potential [V]
χ	External work function [eV]
φ	Work function [eV]
φ_s	Work function component related to surface charge [eV]
φ_{in}	Internal work function component [eV]
[ ]	Square brackets around the symbols of defects denote the concentration in molar fractions

Introduction

Crystalline solids form periodic structures of ions or atoms. However, perfect crystals do not exist. Real crystals contain a wide range of structural imperfections (defects). These imperfections have a substantial effect on the properties of the crystalline solids.

There are several types of imperfections, including *linear defects, planar defects, spatial defects,* and *point defects*. This book is focused on point defects and their effects on the properties of metal oxides. Awareness is growing that properties of nonstoichiometric compounds, including metal oxides, are determined by point defects rather than crystalline structure [1–3]. The defect-dependent properties include electrical properties, mass transport kinetics (diffusion), charge transport kinetics, reactivity, catalytic properties, and light-induced properties, such as photoreactivity.

This book considers the relationships between the concentration of point defects and the properties of binary metal oxides. The focus is on titanium dioxide, TiO_2, owing to its increasing importance in a range of environmentally friendly applications.

So far, TiO_2 has been applied mainly as a pigment for paints, paper, and plastics. In 1972, the pioneering work of Fujishima and Honda [4] reported for the first time that TiO_2 may be used as a photoelectrode for water splitting using solar energy as the driving force of the process. This discovery paved the way for an entirely new application of TiO_2 in solar energy conversion. The discovery by Fujishima and Honda resulted in enormous interest in studies of this compound. Awareness is growing that TiO_2 may soon become a strategic energy-related material in the production of solar hydrogen fuel and photocatalytic water purification. The wide range of applications of TiO_2 has been outlined in the book by Fujishima et al. [5].

It has been shown that the TiO_2 formula is not reflective of the complex composition of this nonstoichiometric compound that involves a range of ionic and electronic point defects [3, 6]. The real chemical formula of TiO_2, which is related to high nonstoichiometry and the associated defect disorder, is complex [3, 6]. It has also been shown that the properties of TiO_2 are closely related to the concentration of ionic point defects (oxygen vacancies, titanium vacancies, and titanium interstitials). These defects may ionize, leading to the formation of electronic defects. Furthermore, interactions between point defects may lead to the formation of larger defect aggregates, such as defect complexes. The picture becomes even more complicated taking into account the presence of aliovalent ions introduced deliberately (dopants) and unintentionally (impurities). Even the presence of impurities at a very low level may have a substantial effect on properties, especially surface composition. The segregation-induced surface enrichment in certain impurities may reach the level of several percents, even if their bulk concentration is at the level of several parts per million [7].

Several functional properties of metal oxides, such as electronic structure, charge transport, reactivity, and photoreactivity, are closely related to defect disorder [6].