

Victor I. Mikla
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Metastable States in Amorphous Chalcogenide Semiconductors

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With 68 Figures

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Preface

This monograph deals with metastable states in amorphous semiconductors – materials which lack long-range periodicity in the atoms' positions, which are in thermodynamic nonequilibrium and which, in addition, have several metastable states. These states give rise to various properties and effects – namely a wide range of photoinduced changes and high photosensitivity and X-ray sensitivity – that are unique among solid-state semiconductors. Historically, amorphous selenium and selenium-based materials have played an important role in physics and technology, and they continue to do so. In these materials there exist inherent intermediate (metastable) states, structural and electronic in origin, which lead to interesting properties and effects different from those of their crystalline counterparts.

In this volume, the metastable states and related effects are investigated in depth against the background of a detailed consideration of local atomic and electronic structure, and taking into account a wide range of light-induced effects.

Although the first publications on amorphous semiconductors date back to the early 1970s, studies of metastable states in these materials had not been analyzed systematically up to now, which led to erroneous ideas, even among specialists. In the present book, experimental investigations of metastable states are reported in detail for elemental selenium and selenium-based materials.

This monograph thus represents a complete course on metastable states in selenium and selenium-based materials, which may be of interest to different groups of readers. On the other hand, it is also intended as a reference book for scientists and engineers who are actively involved in amorphous semiconductor material characterization and defect engineering in research institutes and industrial laboratories. Chapter summaries and tables compiling the theoretical, methodological and experimental results allow quick access to the major results and simple location of detailed information in the text. The data evaluation technique presented here provides insight into the analytical potential of the various techniques, for example Raman scattering, thermally stimulated depolarization currents, and time-of-flight xerographic spectroscopy.

Concerning manuscript preparation, I am grateful to Dr. Angela Lahee for her helpful comments. We would like to thank the language editor, Deborah Hollis, for her very expert work. Finally, I would like to express my deepest thanks to my wife, Ottilia, for her unfailing support and patience, and for understanding that compiling a monograph requires much time.

Uzhgorod
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Victor I. Mikla

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Acronyms and Abbreviations/Symbols

CTL	Charge transport layer
dc	Direct current
EXAFS	Extended X-ray absorption fine structure
FSDP	First sharp diffraction peak
FTIR	Fourier transform infrared
IR	Infrared
IVAP	Intimate valence alternation pair
Nd:YAG	Neodymium-doped yttrium aluminium garnet
PD	Photodarkening
PGL	Photogeneration layer
PIDC	Photoinduced discharge curve
PMMA	Poly(methylmethacrylate)
TOF	Time-of-flight
TSC	Thermally stimulated conductivity
TSDC	Thermally stimulated depolarisation current
VAP	Valence alternation pair
XRD	X-ray diffraction
2D	Two-dimensional

C	Capacitance
d	Sample thickness
E_g	Energy gap
E_g^T	Tauc gap
E_t	Thermal activation energy
E_{th}	Threshold energy density
E_σ	Conductivity activation energy
G	Conductance
h	Planck constant
I	Intensity
I_{ph}	Photocurrent
J_D	current density

k	Boltzmann constant
N_v	Density of states in the valence band
n	Refractive index
P	Power density
p	Concentration of free holes in the valence band
Q_0	Initial charge
R	Reflectance
R_c	Structural correlation length
S	Capture cross section
T	Temperature; transmission
T_g	Glass transition temperature
T_{rel}	Relative transmissivity
t	Time
t_T	Transit time
U	Voltage
U_r	Residual voltage
V	Velocity of sound; voltage
ν_T	Heating rate
α	Absorption coefficient
ϵ	Dielectric constant
$\zeta(\tau)$	Relaxation function
η	Diffraction efficiency
Θ	Angle
Λ	Grating pitch
λ	Wavelength
μ	Mobility
σ	dc conductivity
τ	Dark-resting time
τ_{MR}	Monomolecular recombination time
χ	Permittivity
$\psi(\tau)$	Relaxation function
ω	Frequency [cm^{-1}]
ω_{max}	Frequency of the peak maximum

Chapter 1

Introduction

Investigation of noncrystalline semiconductors is one of the most interesting and attractive disciplines of condensed matter physics. In fact, these investigations are strongly stimulated by both scientific and technological factors. Such materials are free of limitations inherent to their crystalline counterparts with long-range order of the positions of the atoms. They have a wide range of applications as given below.

The intellectual attractiveness of noncrystalline semiconductors is explained by new approaches. The latter are not connected with the terminology of the Brillouin zone, selection rules and steric arguments, which are not applicable to disordered (noncrystalline) systems. Another reason that makes new approaches necessary is connected with the absence of long-range order. In fact, most conventional techniques typically used for classical crystalline semiconductors are complicated to realize at conditions in which the carrier range is of the order of interatomic distances and/or when the interpretation of experimental data is ambiguous. In addition, conventional spectroscopic techniques give structureless spectra without clear features that would help in understanding fundamental properties.

Amorphous (vitreous) chalcogenides are materials containing one or more chalcogenide elements (group VI in the periodic table, e.g. sulfur, selenium or tellurium) as a substantial constituent. They are covalently bonded materials and may be classified as a molecular solid. It is important to emphasise that they behave like semiconductors.

The unique properties of this class of materials are explained by structural disorder, thermodynamic nonequilibrium and metastability. The designation *metastable state* is reserved for states whose lifetimes are relatively long. Metastability is a general scientific concept that describes states of delicate equilibrium. A system is in a metastable state when it is in equilibrium but is susceptible to fall into a lower-energy state with only slight interaction. This may be bandgap illumination, and/or annealing. A metastable state is thus considered a somewhat stable intermediate stage of a system, the energy of which may be lost in discrete amounts. For example, many chalcogenides exhibit a light-driven metastability called photodarkening. Photodarkening is a reduction in bandgap on exposure to light. The physical origin of the process, which takes place during various structural transformations induced by bandgap light and thermal annealing, remains unclear. It is necessary to note that quasi-stationary states – the initial and final, after the corresponding