

The interaction between light and electrons in semiconductors forms the basis for many interesting and practically significant properties. This book examines the fundamental physics underlying this rich complexity of photoelectronic properties of semiconductors, and will familiarise the reader with the relatively simple models that are useful in describing these fundamentals. The basic physics is also illustrated with typical recent examples of experimental data and observations.

Following introductory material on the basic concepts, the book moves on to consider a wide range of phenomena, including photoconductivity, recombination effects, photoelectronic methods of defect analysis, photoeffects at grain boundaries, amorphous semiconductors, photovoltaic effects and photoeffects in quantum wells and superlattices. The author is Professor of Materials Science and Electrical Engineering at Stanford University, and has taught this material for many years. He is an experienced author, his earlier books having found wide acceptance and use. This book represents, as much as any one book can, his 44 years of research to date.

Readers will therefore find this volume to be an up-to-date and concise summary of the major concepts, models and results. It is intended as a text for graduate students, but will be an important resource for anyone researching in this interesting field.



Photoelectronic properties of semiconductors



Photoelectronic properties of semiconductors

RICHARD H. BUBE

Professor of Materials Science and Electrical Engineering Stanford University





> Published by the Press Syndicate of the University of Cambridge The Pitt Building, Trumpington Street, Cambridge CB2 1RP 40 West 20th Street, New York, NY 10011-4211, USA 10 Stamford Road, Oakleigh, Victoria 3166, Australia

© Cambridge University Press 1992

First published 1992

A catalogue record of this book is available from the British Library

Library of Congress cataloguing in publication data

Bube, Richard H., 1927-

Photoelectronic properties of semiconductors/Richard H. Bube.

p. cm

Includes bibliographical references.

ISBN 0-521-40491-6.—ISBN 0-521-40681-1 (pbk.)

1. Semiconductors. 2. Photoelectronics. I. Title.

TK7871.85.B83 1992

621.381'52—dc20 91-20942 CIP

ISBN 0 521 40491 6 hardback ISBN 0 521 40681 1 paperback

Transferred to digital printing 2004

UY



> Ever since the creation of the world His invisible nature, namely, His eternal power and deity, has been clearly perceived in the things that have been made.

Romans 1:20-(RSV)



Contents

	Preface	XVII
1	Introductory concepts	1
	1.1 Overview	1
	1.2 Intrinsic optical absorption	7
	1.3 Extrinsic optical absorption	9
	1.4 Electrical contacts	10
	Blocking contacts	11
	Ohmic contacts	14
	Single injection	15
	Double injection	17
2	Photoconductivity parameters	18
	2.1 Overview	18
	2.2 Measures of photosensitivity	20
	Specific sensitivity	20
	Detectivity	20
	Photoconductivity gain	21
	2.3 Spectral response of photoconductivity	21
	2.4 Speed of response: effect of traps	26
	Decrease in speed of response	27
	Decrease in drift mobility	27
	Decrease in photosensitivity	28
	2.5 Simple kinetics: intrinsic semiconductor	28
	Insulator case	29
	Semiconductor case	30
	2.6 Maximum gain	30
	2.7 Types of photoconducting systems	31
	Homogeneous material	31



x Contents

	p-n junctions	33
	n-p-n junctions	35
	Polycrystalline intergrain barriers	36
	2.8 Mathematical models for photoconductivity	39
	Complete mathematical model	39
	Steady-state Fermi levels	41
	Demarcation levels	42
3	One-center recombination models	45
	3.1 The simplest one-center model	45
	n-equation in steady state	46
	p-equation in steady state	47
	Qualitative evaluation	47
	Specific solutions: n-equation	47
	Specific solutions: p-equation	48
	A simple computer approach	49
	3.2 Insulator model including thermal processes	50
	3.3 General large-signal model	50
	3.4 Model for sublinear behavior without traps	52
	3.5 One-center model with traps	56
4	The Shockley-Read one-center model	60
	4.1 General properties of the model	60
	4.2 Case A: small signals, equal lifetimes	62
	4.3 Case B: large signals, equal lifetimes	64
	4.4 Case C: small signals, unequal lifetimes	65
	4.5 Case D: large signals, unequal lifetimes	65
	4.6 Comparison with computer model calculations	67
	4.7 Two Shockley-Read recombination centers	67
5	Two-center recombination effects	71
	5.1 Two-center phenomena	71
	Imperfection sensitization	72
	Supralinear photoconductivity	73
	Thermal quenching	76
	Optical quenching	76
	Negative photoconductivity	79
	Photoconductivity saturation with illumination	
	intensity	80
	5.2 A qualitative two-center model	81
	5.3 Examples of sensitizing imperfections	82
	5.4 Fermi level and demarcation level analysis	83



	Conte	nts	xi
	5.5	Negative photoconductivity	87
	5.6	Photoconductivity saturation with increasing pho-	
		toexcitation rate	89
	5.7	A simple analytical two-center model	91
		Low photoexcitation rate: beginning of supra-	
		linear photoconductivity	93
		High photoexcitation rate: end of supralinear	
		photoconductivity	94
	5.8	Calculations with the general model	94
	5.9	Specific examples	96
		Identifying the sensitizing center	96
		Sensitizing centers in solid solutions	98
		High impurity concentration effects	99
		Silicon single crystals with Zn impurity	101
6	Reco	mbination processes	105
	6.1	Radiative recombination	105
		Intuitive approach	105
		Detailed balance for intrinsic recombination	106
		Dipole approximation	106
	6.2	Phonon emission: Coulomb attractive	
		imperfection	108
		Simplest model	108
		Drift equal to diffusion	108
		Cascade capture with multiphonon emission	109
	6.3	Coulomb repulsive imperfection	110
	6.4	Non-radiative recombination: Auger	111
	6.5	Summary of recombination cross sections	113
7	Stead	y state photoelectronic analysis	114
	7.1	Temperature dependence of dark conductivity	114
	7.2	Dark Hall effect	116
	7.3	Dark thermoelectric effect	117
	7.4	Dark Schottky barrier capacitance	118
	7.5	Optical absorption	119
	7.6	Photoconductivity	119
	7.7	Minority carrier lifetime	120
		Photoconductivity saturation with electric field	120
		Photomagnetoelectric effect	121
		Surface photovoltage	122
		Electron- and photon-beam-induced current	123
		Spectral response of junctions	123



xii Contents

	Steady-state photocarrier grating technique	124
	Transient methods	124
	7.8 Photo-Hall effects	124
	Change in scattering cross section by	
	photoexcitation	125
	Effects associated with optical quenching	127
	Effects associated with temperature depend-	
	ence of lifetime	129
	Persistent effects in high-resistivity GaAs	132
	7.9 Photothermoelectric effects	134
	7.10 Photocapacitance	136
	7.11 Luminescence	141
	Luminescence analysis of ZnSe: Cu crystals	143
8	Transient photoelectronic analysis	149
	8.1 Representative decay measurements	149
	Exponential decay rate	150
	Strong retrapping	150
	Rate window	151
	Thermally stimulated behavior	151
	8.2 Decay of a single level	151
	τ constant; no retrapping; neglect dn/dt	152
	τ not constant; no retrapping; neglect dn/dt	153
	τ constant; no retrapping; include dn/dt	153
	8.3 Strong retrapping	153
	Trap above Fermi level; $E_t > E_{Fn}$	154
	Trap below Fermi level; $E_t \ll E_{Fn}$	154
	τ not constant; $E_{\rm t} > E_{\rm Fn}$	155
	Trap analysis using a strong retrapping	
	perspective	155
	Intermediate retrapping	155
	Rise curves	156
	8.4 Specific trap distributions	156
	Discrete set of traps	156
	Continuous uniform trap distribution	157
	Continuous exponential trap distribution	160
	8.5 Thermally stimulated luminescence	163
	8.6 Thermally stimulated conductivity	167
	Discrete trap level; no retrapping	169
	Discrete trap level; strong retrapping	170
	'Decayed TSC' measurement	171



	Contents	xiii
	Hall effect during thermal stimulation	172
	8.7 A mystery story: 'photochemical changes'	175
	8.8 Photoinduced transient spectroscopy	180
	8.9 Deep level transient spectroscopy	182
9	Photoeffects at grain boundaries	189
	9.1 Small grain vs large grain effects: CdTe films	190
	9.2 Direct measurements of grain boundary pro-	
	perties: CdTe films	193
	9.3 CdS films	196
	Heat treatment in hydrogen	197
	O ₂ adsorption effects	199
	Effect of dc electric field during heat treatment	201
	9.4 PbS films	204
	Effects of O ₂ adsorption and desorption in the	
	dark	205
	Photoconductivity	207
	Effects of O ₂ adsorption: time dependence	211
10	Amorphous semiconductors	216
	10.1 Background information on amorphous	
	semiconductors	217
	Preparation	217
	Types of amorphous materials	217
	General description	217
	10.2 Amorphous chalcogenides	219
	General photoconductivity characteristics	219
	Photoconductivity model: type I	
	photoconductivity	222
	Scaling of parameters	230
	Other transport properties	232
	How many data are required to establish a	
	model?	232
	10.3 Hydrogenated amorphous Si (a-Si:H)	233
	Optical determination of defect densities	233
	Effects of illumination on a-Si:H	235
	Photoconductivity model	235
	Doping of a-Si: H	239
	Optical degradation	241
11		244
	11.1 Types of semiconductor junctions	244
	Homojunctions	245



xiv Contents

		Heterojunctions	246
		Buried or heteroface junctions	247
		Schottky barriers	247
		p-i-n junctions	248
	11.2	Simple photovoltaic model	250
	11.3	A more realistic photovoltaic model	252
		Junction current	252
		Collection functions	253
		Other photovoltaic parameters	255
	11.4	Junction transport processes in heterojunctions	256
		Diffusion	257
		Recombination in the depletion region	257
		Interface recombination without tunneling	257
		Tunneling limited recombination through in-	
		terface states withut thermal assistance	258
		Thermally assisted tunneling through interface	
		barrier	258
	11.5	Photovoltaic materials	260
	11.6	Cu _x S/CdS heterojunctions: theater for photo-	
		electronic effects	262
		Overview of effects	262
		Junction capacitance	263
		Spectral response	263
		Optical quenching	264
		Persistence of enhancement	265
		Enhancement/quenching model	265
		Photocapacitance effects	267
		Thermally restorable optical degradation	
		(TROD)	270
12	Quanti	um wells and superlattices	280
	12.1	Electron in a one-dimensional well	281
	12.2	Effective mass filtering photoconductor	282
	12.3	Avalanche photodiodes (APDs)	283
		Multiquantum wells	284
		Staircase structures	284
		Channeling structures	287
		Impact ionization across the band discontinuity	287
	12.4	Quantum well infrared photodetectors	289
	12.5	Quantum confined Stark effect devices	290
		High-speed modulation of a light beam	292



Contents	
Wavelength-selective voltage-tunable photo-	
detector	293
Self electro-optic effect devices	294
12.6 Internal electric polarization of quantum wells	294
12.7 Tunable band-edge discontinuities	297
Doping interface dipoles	297
Ultrathin intralayers	300
12.8 Tunneling-related phenomena	301
Sequential resonant tunneling	301
Far infrared laser	303
Wavelength-selective infrared photodetector	305
Notes	306
Bibliography	313
Index	315



Preface

My earlier book, *Photoconductivity of solids*, published in 1960 and subsequently in print for 26 years, attempted to describe all of the previous work related to photoconductivity or any of its associated phenomena. From the response that it evoked it appears that this attempt was reasonably successful.

But the field continued to expand rapidly. If a thousand references were adequate to describe almost a century from Willoughby Smith's discovery of photoconductivity in selenium in 1873, tens of thousands of references have been added in recent years. A representative bibliography of books and reviews is included at the end of the text. In 1976 when *Photoconductivity and related phenomena*, edited by J. Mort and D. Pai was published, fifteen authors contributed to cover a wide variety of solids in addition to crystalline semiconductors, like molecular crystals, amorphous materials, polymeric photoconductors, and non-polar liquids, which had been mentioned either not at all or very little in *Photoconductivity of solids*. It is no longer possible for a single, reasonably long monograph to provide a complete discussion of the whole field.

So it is not the purpose of this book even to attempt to give an exhaustive treatment of all photoelectronic phenomena in semiconductors. Rather it is the purpose to provide a look at the fundamentals that underlie the rich complexity of phenomena, to provide the reader with some familiarity for relatively simple models that are useful in describing these fundamentals, and to give typical recent examples of experimental data and observations that illustrate them. The present book deliberately chooses to limit itself to photoelectronic properties of semiconductors, still a very large and rapidly growing field indeed,



xviii Preface

especially when one realizes the potential of low-dimensional structures such as quantum wells and superlattice structures.

It has been a special thrill for me to be able to write this book, in a kind of way reliving and at the same time updating my professional research career. My purpose in writing the book is facilitated by the fact that for the past 30 years I have been teaching courses related to this subject area at Stanford University. I would like to express my gratitude toward all those friends and colleagues through the years who have contributed to my progress, and to all of my students (Ph.D. No. 50 graduated in 1990) involved in research with me, as well as to those many more who interacted in the courses taught at Stanford and thereby directly or indirectly contributed to the material of this book.

I was in the midst of the task of writing the book, when I learned of the death of Dr Albert Rose, who was my professional mentor and friend particularly during the 14 years I spent at the RCA Laboratories. I wish to acknowledge my special indebtedness to him.

My beloved wife Betty was by my side through the writing of the original *Photoconductivity of solids*, and I thank God that I have had her unfailing love and support through all the intervening years.

Richard H. Bube Stanford University Stanford, California