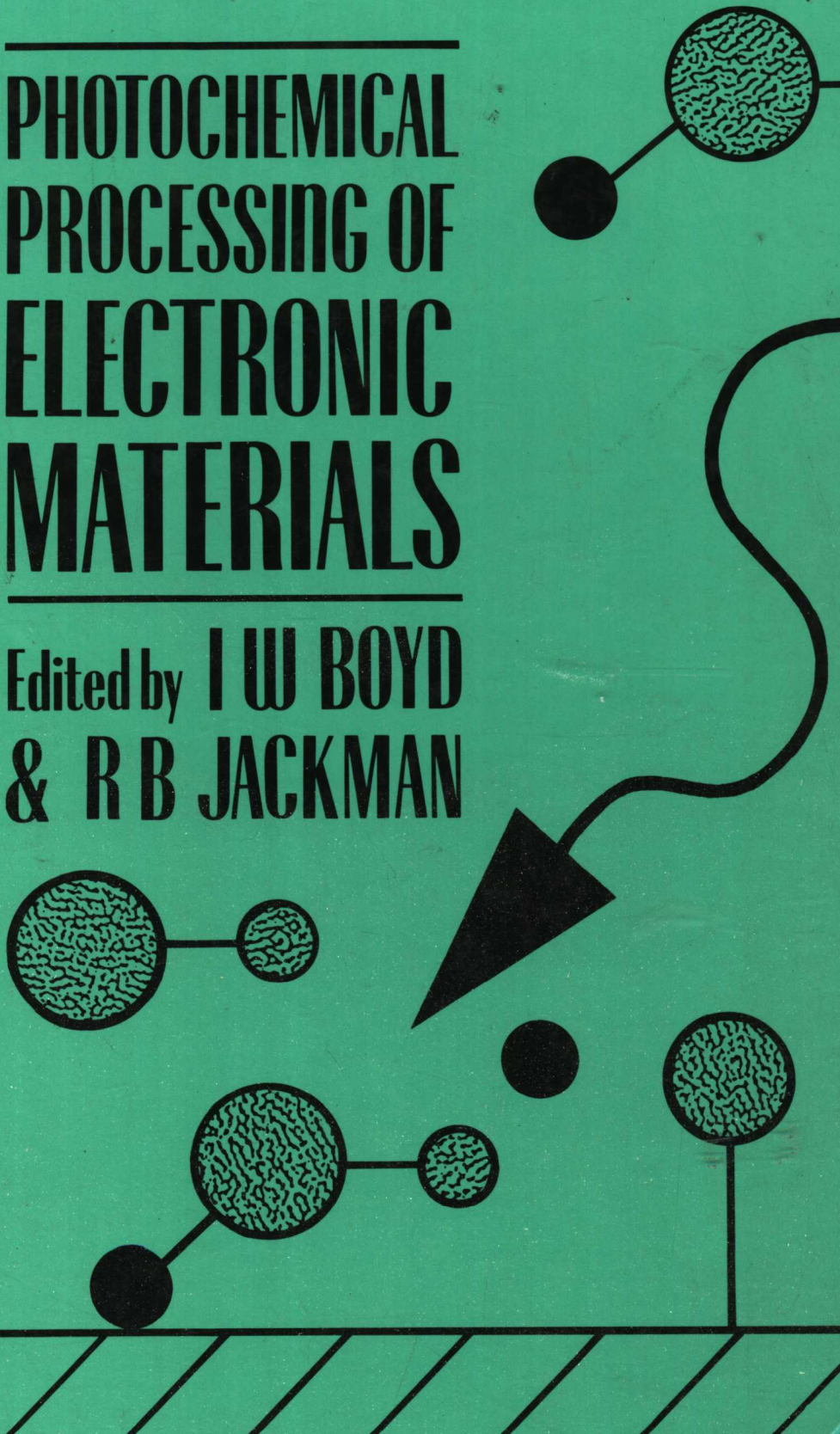

PHOTOCHEMICAL PROCESSING OF ELECTRONIC MATERIALS

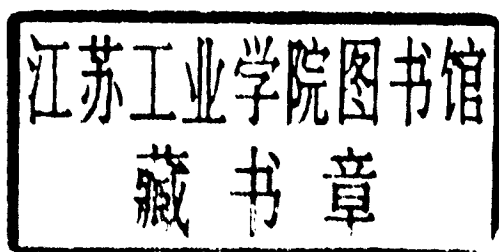
Edited by I W BOYD
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Photochemical Processing of Electronic Materials

Edited by
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Preface

The rapid and efficient physical processes that lasers are capable of performing have already resulted in a steady increase since the early 1970s in applications on various production lines worldwide. These include machining, welding and alloying, surface hardening, insulation stripping, and impurity or defect gettering. It is the novel and unique processing characteristics presented by lasers that give rise to operating conditions never previously available, and thus the great variety of applications.

Lasers, and more generally lamps, can also give rise to a myriad of chemical reaction steps. The nature of light is such that the discrete quanta associated with particular emissions can selectively drive a key step in the reaction ladder leading to some surface modification or material removal, or to the formation of a thin film. The radiation can also be transformed into heat and drive a range of thermally controlled phenomena. These regimes of photochemical processing of electronic materials, have historically been largely unexplored, and only within the last decade have they begun to attract sizeable worldwide interest. The burgeoning of the field has been most evident at international level during events organized under the auspices of the Materials Research Society (MRS) and the European EMRS—societies whose remit is to foster and encourage interdisciplinary science.

It is intended that this new volume complement and update the existing work already published in this field. In this respect, the main concepts and basic principles are restricted to one introductory chapter. The following 17 chapters tackle specific and specialized areas of research that are currently being studied on a worldwide scale. This book contains reviews on UV lens design, laser lithography with respect to other lithographic techniques, photo-nucleation, excimer laser development, incoherent lamp applications, and *in situ* laser characterization; topics that have not been

reviewed or assessed before in such detail. Together with articles on precursors for direct writing, laser ablation (of polymers and of superconductors), laser doping, etching, deposition and growth, it is hoped that this is a valuable and unique contribution to the field. It is aimed not only at both active and new researchers in the area, but also at those who feel they could be potential users of the technology.

This volume evolved from the 5th UK Photochemical Processing Workshop, a three-day meeting held at University College London (UCL) that was strongly supported by the EMRS/EEC Network on Laser Chemistry. The workshop was co-sponsored by several other learned societies, namely the British Association of Crystal Growth, the Institute of Physics, the Institution of Electrical Engineering, and the Royal Society of Chemistry. It additionally benefited from support from the EEC/Science programme on Photoprocessing of GaAs, the European Office of the United States Air Force, and several industries, whose inspiration and generosity is gratefully acknowledged.

The editors would like to take this opportunity to thank many people who have assisted, not only towards this volume, but also in the development of understanding in the field over the years. In particular, we are grateful to the authors of the chapters for delivering their erudite contributions (essentially) on time! Very special thanks go to our closest colleagues in the laboratory at UCL, F. Beech, B. Bradley, T. Kerr, P. Patel and G. Tyrrell, without whose help this project would have floundered at the first hurdle.

Finally, we should both like to take this opportunity to admit our indebtedness to our wives and families, who have so patiently tolerated the eccentricities of the British academic over the past years.

Ian W. Boyd
Richard B. Jackman

*University College London
July 1991*

Contents

Contributors	xi
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Preface	xv
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1 Photochemical Processing: Fundamental Mechanisms and Operating Criteria

IAN W. BOYD

1.1 Introduction	1
1.2 Photon sources	2
1.3 Photo-excitation of matter	8
1.4 Adsorption	19
1.5 Laser-induced heating	22
1.6 Nucleation and growth	24
1.7 Chemical reactions and growth rates	26
1.8 Modes of photochemical processing	31
1.9 Summary	37
References	37

2 Developments in Excimer Lasers for Photochemical Processing

J. M. GREEN and M. R. OSBORNE

2.1 Introduction	41
2.2 Background	41
2.3 Modern commercial excimer lasers	46
2.4 Excimer laser development	50
2.5 Conclusions	63
References	63

3 Deep UV Optics for Excimer Lasers

F. N. GOODALL

3.1	Introduction	67
3.2	The optimal design problem	68
3.3	General optical design considerations	69
3.4	Lenses for laser chemical processing	71
3.5	Micromachining	74
3.6	Conventional lithography	78
3.7	Conclusions	81
	References	82

4 Submicron Lithography for Semiconductor Device Fabrication

R. A. LAWES

4.1	Introduction	83
4.2	Optical lithography	84
4.3	X-ray lithography	89
4.4	Scanning electron beam lithography	93
4.5	Focused ion beams	98
4.6	Summary	102
	References	103

5 Promoting Photonucleation on Semiconductor Substrates for Metallization

J. FLICSTEIN and J. E. BOURÉE

5.1	Introduction	105
5.2	Basics: phenomena and mechanisms	106
5.3	Photonucleation from gas phase and surface-adsorbed precursors	119
5.4	Spatial localization of clusters	126
5.5	Kinetic models of photonucleation	128
5.6	Important future issues	136
	Acknowledgements	138
	References	139

6 Considerations of the Microscopic Basis for Photon-Enhanced Chemical Beam Epitaxy

J. S. FOORD

6.1	Introduction	143
6.2	Reaction mechanisms for thermal CBE	145

6.3	Photodesorption and photoreaction of molecules at surfaces	151
6.4	Possibilities for photo-CBE	153
6.5	Conclusions	155
	References	156
 7 Photo-Assisted II–VI Epitaxial Growth		
S. J. C. IRVINE, H. HILL, J. E. HAILS, G. W. BLACKMORE and A. D. PITT		
7.1	Introduction	159
7.2	Photon–vapour interactions	160
7.3	Photon–surface interactions	162
7.4	Experimental	163
7.5	Macroscopic photo-enhanced CdTe growth	164
7.6	Modelling of surface kinetics	168
7.7	Microscopic photo-enhancement	169
7.8	Superenhancement	176
7.9	Conclusions	179
	Acknowledgements	180
	References	180
 8 IR and UV Laser-Induced Deposition of Hydrogenated Amorphous Silicon		
PETER HESS		
8.1	Introduction	181
8.2	Laser excitation and chemistry	185
8.3	Kinetics and growth	192
8.4	Material properties	195
8.5	Deposition by direct substrate illumination	202
8.6	Optimized material for applications	204
8.7	Conclusions	206
	Acknowledgements	208
	References	208
 9 UV Lamp Deposition of a-Si:H and Related Compounds		
W. I. MILNE and P. A. ROBERTSON		
9.1	Introduction	211
9.2	Mercury-sensitized deposition	212
9.3	Direct photo-CVD	215
9.4	Direct photo-CVD using an internal lamp	221

9.5	Material properties	225
9.6	Conclusions	230
	References	230
10	UV Photo-Assisted Formation of Silicon Dioxide	
	ERIC FOGARASSY	
10.1	Introduction	233
10.2	Processing modes and basic techniques	234
10.3	Conclusions	253
	References	254
11	Gas Immersion Laser Doping (GILD) in Silicon	
	FRANÇOIS FOULON	
11.1	Introduction	257
11.2	Laser-assisted doping techniques	260
11.3	The mechanisms of the GILD technique	264
11.4	Technological aspects	272
11.5	Doping mechanisms	285
11.6	Conclusions	291
	Acknowledgement	292
	References	292
12	Photochemical Etching of III–V Semiconductors	
	RICHARD B. JACKMAN	
12.1	Introduction	297
12.2	Photochemical etching: the basics	301
12.3	<i>In situ</i> processing	303
12.4	Reaction mechanisms revisited	304
12.5	III–V semiconductor photochemical etching	323
12.6	Concluding remarks	333
	Acknowledgements	334
	References	334
13	Excimer Laser Chemical Etching of Silicon and Copper	
	J. C. S. KOOLS, T. S. BALLER and J. DIELEMAN	
13.1	Introduction	339

13.2	Laser chemical etching of silicon	340
13.3	Laser chemical etching of copper	347
	References	355

14 Laser Ablation of Polymers

P. E. DYER

14.1	Introduction	359
14.2	Basic characteristics	360
14.3	Applications	367
14.4	Lithography	368
14.5	Micromachining	368
14.6	Surface modification	374
14.7	Miscellaneous applications	379
14.8	Discussion	379
	Acknowledgements	380
	References	380

15 Laser Ablation of Electronic Materials

FRANK BEECH and IAN BOYD

15.1	Introduction	387
15.2	Background and theory	389
15.3	Experimental approach	412
15.4	High- T_c films	414
15.5	Summary	425
	References	426

16 Fast *In Situ* Metallization: A Comparison of Several Methods with Possible Applications in High-Density Multichip Interconnects

MARCEL WIDMER, PATRIK HOFFMANN,
BAUDOUIN LECOHER, HERBERT SOLKA,
JEAN-MICHEL PHILIPPOZ and HUBERT VAN DEN BERGH

16.1	Introduction	433
16.2	Laser chemical vapour deposition (LCVD)	435
16.3	Laser-induced decomposition of a solid layer on the substrate	443

16.4	Fast <i>in situ</i> prenucleation followed by selective metal build up	450
16.5	Fast <i>in situ</i> processing by a partial change of the precursor layer	458
16.6	Conclusions	459
	Acknowledgements	460
	References	460
17	Laser-Assisted Fabrication of Integrated Circuits in Gallium Arsenide	
	FRANÇOIS FOULON and MINO GREEN	
17.1	Introduction	465
17.2	Conventional processes	471
17.3	Laser processing	481
17.4	Review of laser projection-patterned processing	486
17.5	Conclusions	494
	References	495
18	Photon Probes for In-Process Control During Semiconductor Fabrication	
	GABRIEL M. CREAN	
18.1	Introduction	501
18.2	Photon–solid interaction	502
18.3	Photon response: modelling and interpretation	503
18.4	<i>In situ</i> probe design considerations and trends	506
18.5	Applications	507
18.6	Conclusions	525
	Acknowledgements	525
	References	526
	Index	529

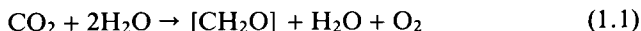
1 Photochemical Processing: Fundamental Mechanisms and Operating Criteria

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1.1 INTRODUCTION

Photo-induced chemical reactions are not only central to everyday events such as photography, photocopying, polymer degradation and the bleaching of dyes, but they also play a vital role in the life support system of the planet. For example, virtually all forms of life are either directly or indirectly dependent upon the photosynthesis of organic compounds from CO_2 and H_2O by



as it is instrumental in initiating the growth of vegetation and producing the O_2 that makes up our atmosphere.

While such reactions must occur in the neighbourhood of light-absorbing pigments such as chlorophyll, many other photoreactions in nature do not require intermediaries to host the event. For example, O_2 within our atmosphere also plays a vital role in shielding us from harmful ultraviolet (UV) radiation from the sun through the following photo-induced reactions:



Nitrogen ions, atoms and molecules similarly undergo a range of photon interactions, by themselves, and also in conjunction with various forms of oxygen.

In reality, a myriad of photo-induced chemical reactions can be initiated, either in the gas phase or within a host solid or liquid. Several of these have

been studied for centuries, while most have only received attention since various intense artificial sources of light have become accessible. The availability of flash lamps not only enables new chemical reactions to be induced, but also allows reaction kinetics to be studied on timescales much less than a second.

The advent of the laser has stretched the list of photo-induced reactions considerably. The range of wavelengths and intensities now available have allowed access not only to new reactions but also to completely new non-linear reaction mechanisms as well as unexplored fields of study. Reaction events down to tens of femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$) can at present be chronicked using laser pulses.

While the vast majority of pioneering studies were performed within the gas phase, around the beginning of the 1980s the use of photons to stimulate reactions that formed thin film layers or delineated patterns on solids began to attract considerable attention [1–4]. Over the past decade, the field has burgeoned and currently sustains several international conferences and workshops each year. Interest in the subject can be found in a wide variety of disciplines, the basic sciences of chemistry and physics, the applied areas of materials and engineering, and the fundamental areas of surface science and quantum electronics. The potential applications are diverse, as the content of this volume testifies.

In this chapter, the reader will be introduced to the basic concepts behind photochemical materials processing. The photon sources used will be described, the underlying mechanisms reviewed, and the processing techniques discussed.

1.2 PHOTON SOURCES

1.2.1 Incoherent sources

For many photo-induced reactions, it is not necessary for the photons to be coherent, i.e. in phase with each other. Nor is it necessary for them to be monochromatic (of a single wavelength). In these instances, photons from a variety of lamps can be used. Such sources may be resistively heated wires (as in a light bulb) or gas discharges (as in a sodium vapour street light). By electrically exciting specific gases or vapours, a range of characteristic discharge spectra can be produced.

Where large continuous powers are desirable, such as for photothermal reactions, current-heated tungsten filaments are commonly used. Arranged in banks, these can produce a steady output at levels approaching 100 kW in a continuum stretching from the near-UV through the visible, peaking in the near-infrared (IR) and falling off into the IR. Indeed, the spectrum is close to that expected from a high-temperature black body. Unavoidable

but gradual evaporation of tungsten atoms can be reduced by adding trace amounts of iodine, which also helps to improve the UV output.

Equally powerful light containing more UV can be acquired from arc lamps, where a gas, or mixture of gases, at medium pressures (450–1500 Torr) is subjected to a large electrical discharge from a capacitor bank. Often, the discharge has to be initiated by pre-ionizing the gas with a very high voltage “trigger”. The light emitted in this case is more characteristic of energy levels available to the ions and atoms of the discharged species. Hg-based vapours are the most widely used, and the greatest emitted intensity usually appears at 365 nm (at efficiencies of up to 6%) along with subsidiary peaks around 300 and 313 nm. Possible lower wavelengths are masked because of self-absorption at these pressures. Such lamps are available commercially at ratings up to 60 kW over several metre column lengths. Higher photon fluxes can be achieved by high-pressure (up to 100 kTorr) short arc lamps. Several kilowatts can be obtained from arc lengths of only centimetres, although the spectrum at these pressures is characterized by only minor features superimposed upon a broad continuum. Hg/Xe mixtures give more spectral detail, especially in the UV; a typical spectrum is shown in Fig. 1.1. Efficiencies even of the strongest lines, however, are no more than 1–2% at best.

Low-pressure lamps (several torr and less) are among the most often used sources today for high-intensity UV light. At these pressures, under a high-voltage discharge, Hg can emit several distinct wavelengths previously self-absorbed. These characteristic lines arise from different atomic transitions:

$$^3P_1 \rightarrow ^1S_0 + 253.4 \text{ nm}, \quad (1.4)$$

$$^1P_1 \rightarrow ^1S_0 + 184.9 \text{ nm} \quad (1.5)$$

and appear at power ratios of about 7:1 for the longer to shorter wavelengths. Under optimum conditions, they can be up to 80% efficient in their conversion of electrical to optical energy. If one retains low-pressure operation, but increases the discharge current to more than 1 A cm⁻², the two characteristic lines saturate, and another line, previously weaker, at 194.2 nm becomes dominant and continues to increase up to current densities beyond 20 A cm⁻². A 1.4 kW Magnetron system can heat Ar atoms, which vaporize Hg to a pressure of 1–2 atm and produce, at efficiencies of greater than 9%, more than 100 W of UV light in each of the 200–260 nm and 260–400 nm regions, as well as 225 W between 400 and 700 nm [5].

Incoherent sources of high intensity deep UV light (<180 nm) are not currently readily available. Hydrogen, deuterium (D₂) and noble gas lamps emit in this region only at modest levels, where, at pressures of less than 2 Torr, several discrete spectral lines can be obtained preferentially over the