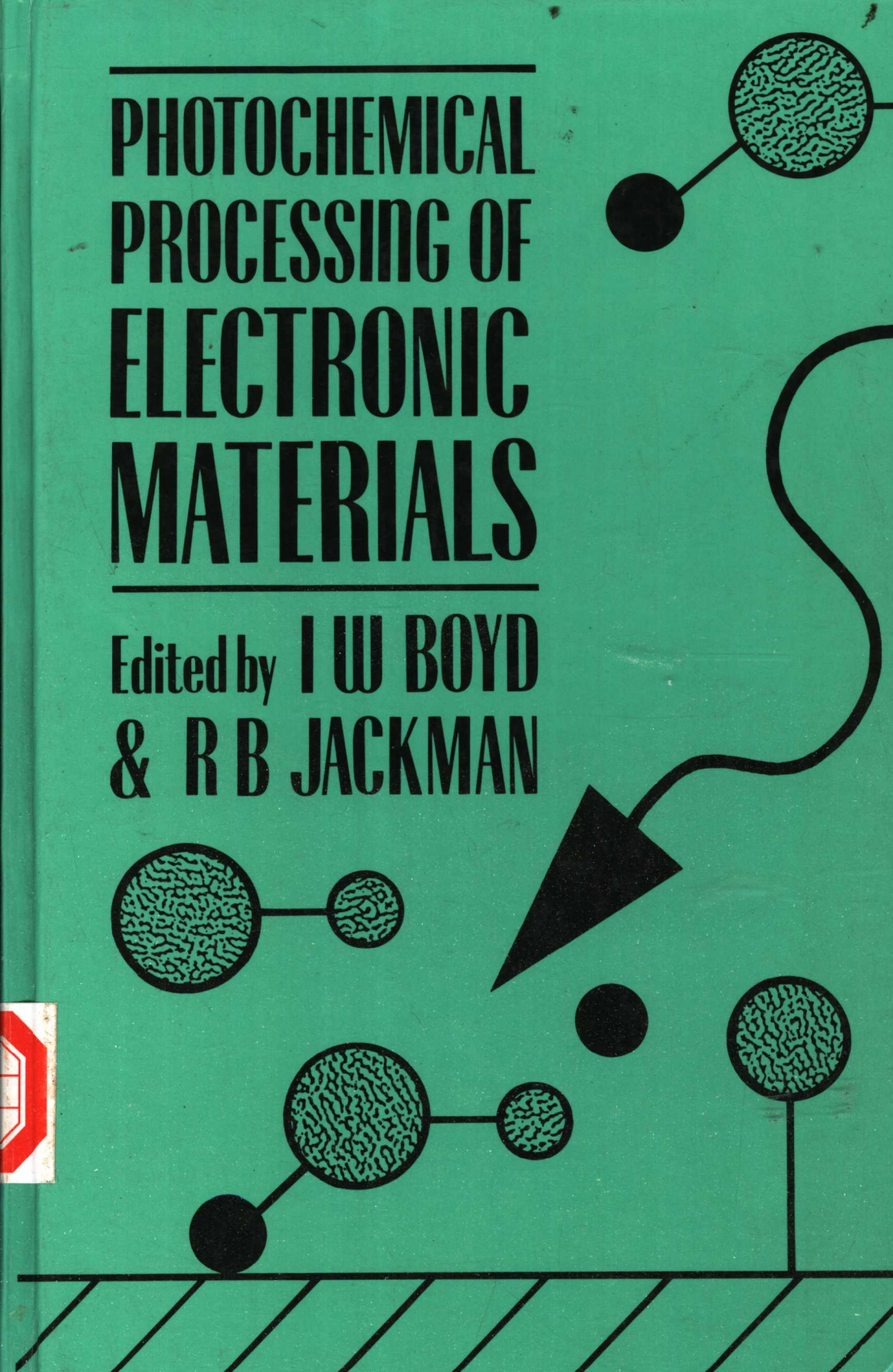
# PHOTOCHEMICAL PROCESSING OF ELECTRONIC MATERIALS

Edited by I W BOYD & R B JACKMAN



# 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

# 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

$$CO_2 + 2H_2O \rightarrow [CH_2O] + H_2O + O_2 \tag{1.1}$$

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:

$$O + UV \rightarrow O^+ + e^- \tag{1.2}$$

$$O_2 + UV \rightarrow O_2^+ + e^- \tag{1.3}$$

$$O_3 + UV \rightarrow O_2 + O \tag{1.4}$$

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

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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 chronicled 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:

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

$$^1P_1 \rightarrow {}^1S_0 + 184.9\ \text{nm} \tag{1.5}$$

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 ($D_2$) 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