Laser Processing and Analysis of Materials

W. W. Duley

York University
Toronto, Ontario, Canada

PLENUM PRESS • NEW YORK AND LONDON

Library of Congress Cataloging in Publication Data

Duley, W. W.
Laser processing and analysis of materials.

Includes bibliographical references and index.
1. Lasers—Industrial applications. I. Title.
TA1677.D84 1982 621.36'6 82-18611
ISBN 0-306-41067-2

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

Printed in the United States of America

Laser Processing and Analysis of Materials

To
my parents

Preface

It has often been said that the laser is a solution searching for a problem. The rapid development of laser technology over the past dozen years has led to the availability of reliable, industrially rated laser sources with a wide variety of output characteristics. This, in turn, has resulted in new laser applications as the laser becomes a familiar processing and analytical tool.

The field of materials science, in particular, has become a fertile one for new laser applications. Laser annealing, alloying, cladding, and heat treating were all but unknown 10 years ago. Today, each is a separate, dynamic field of research activity with many of the early laboratory experiments resulting in the development of new industrial processing techniques using laser technology.

Ten years ago, chemical processing was in its infancy awaiting, primarily, the development of reliable tunable laser sources. Now, with tunability over the entire spectrum from the vacuum ultraviolet to the far infrared, photochemistry is undergoing revolutionary changes with several proven and many promising commercial laser processing operations as the result.

The ability of laser sources to project a probing beam of light into remote or hostile environments has led to the development of a wide variety of new analytical techniques in environmental and laboratory analysis. Many of these are reviewed in this book.

We now stand at a point in the development of laser technology at which one can see clearly a number of areas in which the laser has provided the solution to an outstanding problem. We can also see with clarity the potential areas in which further applications may occur. At present, some other possible applications are only interesting curiosities in the research laboratory.

The purpose of this book is to survey areas in materials science and analysis in which the laser has a proven or potential application. As such, the reader will find that while in one section we will discuss a well-established laser processing technique, in another we may lapse into the consideration of what may

be a prototype laboratory experiment. By adopting this approach, one obtains an overview of a dynamic research field while at the same time seeing which laser applications have proven feasible in an industrial environment.

My own education in lasers and laser technology has been greatly aided by contacts with colleagues and students. Production of this book would have been impossible without the expert typing of Mrs. Gladys Hayward, the drawing skill of Sally Lakdawala, and the photographic expertise of Bryson Timmins. Thanks also to Elisa Bourdon for her careful reading of parts of the manuscript.

I am also indebted to all those who freely granted permission to quote and reproduce various parts of their work.

Finally, my thanks go to my wife, Irmgardt, and my sons, Nick and Mark, for their encouragement and support during the writing and production of this book.

Toronto Walter W. Duley

Contents

1 Lasers and Laser Radiation

3 Laser Processing of Semiconductors

4 Chemical Processing

5 Lasers in Chemical Analysis

6 Lasers in Environmental Analysis

Chapter 1

Lasers and Laser Radiation

1.1. INTRODUCTION

This chapter surveys commercially available lasers and discusses some characteristics of laser radiation that make it useful in the processing and analysis of materials. Performance data for commercial versions of the most widely applied laser sources are outlined. The aim of this summary is to provide ready access to information that may be required in the assessment of the viability of particular laser applications. With this object in mind, the use of ancillary beam handling and measuring components is discussed from a practical point of view. The important problem of beam focusing is discussed in some detail.

Within this chapter, emphasis has been placed on providing the reader with easy access to data pertaining to the generation and use of laser radiation. Data presented are typical of commercially available systems and components, but the performance of laboratory prototype systems may be significantly better. However, it is hoped that by providing performance data representative of commercially available systems the reader will be able to assess the applicability of a particular laser system to the solution of a specific problem.

1.2. LASER SOURCES

1.2.1. Ruby Laser

Ruby is formed when a small amount of Cr_2O_3 is dissolved in sapphire, Al_2O_3. The pink color is due to absorption by Cr^{3+} ions in the broad bands that provide pumping for the red laser transitions. Energy levels for $Cr^{3+}:Al_2O_3$ are shown in Figure 1.1. Pumping occurs by absorption in the broad $^4A_2 \rightarrow {}^4T_2$, $^4T_1$ bands. This is followed by an efficient radiationless deactivation to the ^2E state. This state is split into two sublevels by the trigonal field distortion at the site of the Cr^{3+} ion. Laser emission occurs from the lower of these, $\bar{E}$, to the ground state. The wavelength of this line, the $\bar{E} \rightarrow {}^4A_2$ transition, is 694.3 nm

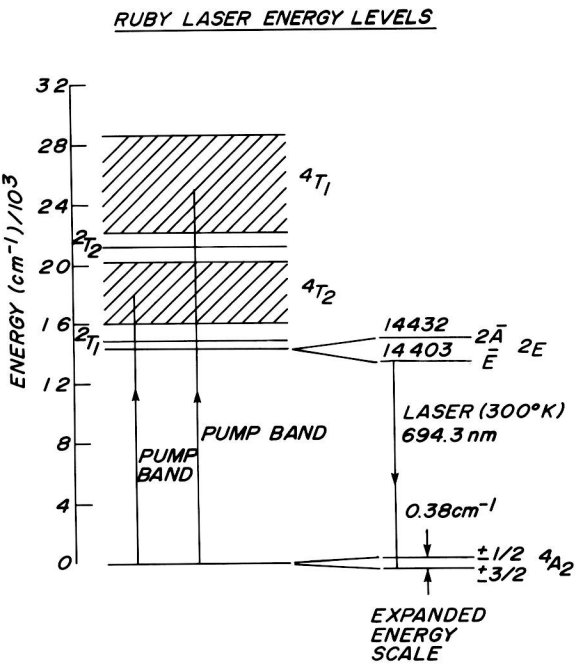

Figure 1.1. Energy levels for Cr^{3+} in ruby.

at room temperature. The ground-state zero-field splitting of 0.38 cm^{-1} is usually contained within the laser linewidth at 300 K.

By using frequency discriminating devices in the laser cavity, the laser can be operated on the $2\bar{A} \rightarrow {}^4A_2$ transition at 692.9 nm at room temperature. Both the R_1 694.3-nm and R_2 692.9-nm lines can be tuned over a $\sim$50-cm^{-1} range by varying the temperature between 77 and 500 K. Widths of the R_1 and R_2 lines also are a function of temperature and become large at temperatures exceeding 100 K.

Typical Cr^{3+} concentrations in ruby are 0.01–0.5 at. %. Since the $Cr^{3+}:Al_2O_3$ system is a three-level laser, population inversion is obtained only when about 50% of Cr^{3+} ions are excited to the ^2E state. This implies a relatively high threshold for oscillation and sensitivity to cavity losses. A summary of optical properties for ruby laser material is given in Table 1.1.

Ruby lasers can be operated in either pulsed or continuous wave (CW) modes. The low overall efficiency ($\sim$0.1%) makes CW operation uneconomical when compared to other CW solid-state lasers. When operated in a pulsed mode without Q-switching, the output of the ruby laser consists of repetitive spikes each of high peak power and $\sim$1 μs duration. Spiking occurs because stimulated emission rapidly depletes the population in the ^2E state while the

Table 1.1. Properties of Ruby Laser Material at 300 K[a]

Cr^{3+} concentration	1.6×10^{19} cm^{-3}
Wavelength	694.3 nm
Stimulated emission cross section	2.5×10^{-20} cm^2
Inversion for 1% gain per cm length	4.0×10^{17} cm^{-3}
Stored energy for 1% gain per cm length	2.3 J cm^{-3}
Loss coefficient	$\sim$0.001 cm^{-1}
Fluorescent lifetime	3 ms
Fluorescent linewidth	0.53 nm
Rod length	2–25 cm
Rod diameter	1 cm

[a]After Weber (1979).

pumping rate to this level is relatively small. Hence the output oscillates spontaneously between "on" and "off" conditions. The laser output commences $\sim$0.5 ms after initiation of the pump pulse and continues for the duration of the pump pulse. This is typically several milliseconds. Maximum repetition rates are usually several ppm and are limited by heating of the laser rod.

Some output characteristics of the ruby laser are summarized in Table 1.2. Parameters are listed for each of the three pulsed modes of operation: long-pulsed, Q-switched, and mode-locked. No entry is given for a CW ruby laser

Table 1.2. Output Characteristics of Ruby Lasers

Pulse length: 1–3 ms	
Output energy	100 J/pulse (multimode) 1 J/pulse (TEM_{00})
Repetition rate	$\lesssim$1 Hz
Divergence	$\sim$5 mrad (multimode) $\sim$1 mrad (TEM_{00})
Beam diameter	1 cm
Peak power in spike	10^6–10^8 W
Pulse length: $\sim$10 ns	
Output energy	1–25 J/pulse (TEM_{00})
Repetition rate	$\lesssim$1 Hz
Divergence	0.3–0.5 mrad
Beam diameter	1 cm
Peak power	10^9 W
Pulse length: 20 ps	
Output energy	10 mJ/pulse (TEM_{00}) 40 mJ/pulse (multimode)
Repetition rate	4 ppm
Divergence	0.2 mrad
Beam diameter	0.2 cm
Peak power	10^8–10^9 W

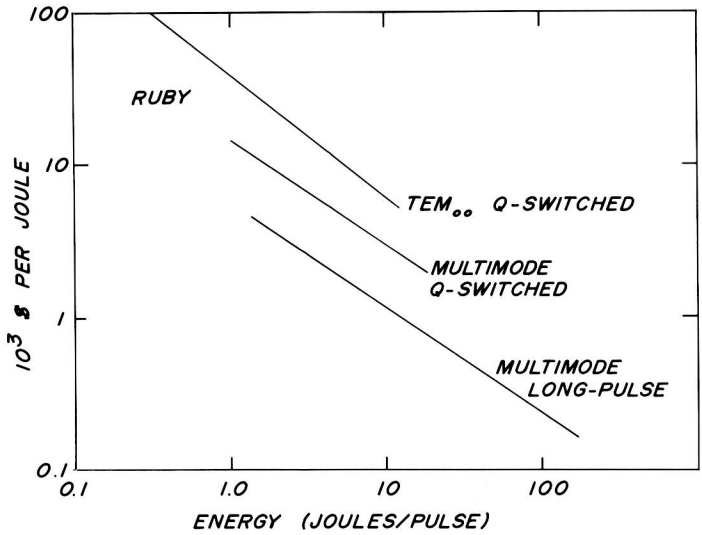

Figure 1.2. Cost per output joule for ruby lasers vs. output energy (1980 dollars).

since such a device does not appear to be commercially available. Pumping of the ruby laser is usually via helical or linear xenon flashlamps although Hg lamps are also used.

Figure 1.2 shows current (1980) costs per output Joule for long-pulse and *Q*-switched ruby lasers. These costs are representative of those quoted by manufacturers in the 1980 edition of the *Laser Focus Buyers Guide*. Some manufacturers offer prepacked frequency doubling to 347 nm on ruby laser systems.

1.2.2. Nd–YAG Laser

The Nd–YAG laser is the most widely utilized of all solid-state lasers. It is available in both pulsed and CW configurations. Many of the characteristics that make this laser attractive in terms of output power, pulse repetition rate, and pulse energy derive from the properties of the yttrium aluminum garnet (YAG) host. Large YAG crystals of high optical quality are readily available and the relatively large thermal conductivity together with four-level operation make high average output powers feasible. The relevant energy levels of Nd^{3+} in YAG are shown in Figure 1.3.

The complexity of the spectra of the rare earth ions in solids is due to the fact that possible $4f^n$ electronic configurations yield many electronic states with energies in the range $\lesssim$30,000 cm^{-1}. Spin–orbit interaction further splits these energy levels.

As the $4f$ electrons in the rare earth ions are shielded by electrons in outer shells, $f \rightarrow f$ transitions are sharp, even when these ions are in a solid-state environment. Transition energy is therefore not highly sensitive to the nature of the host crystal. However, static crystal field effects introduce some splitting of crystal field levels. As a result, the levels in the energy diagram of Figure 1.3 are shown as broad bands. In reality, each of these bands contains a number of discrete energy levels.

The laser line at 1064 nm is the transition in Nd–YAG with lowest pump threshold. It corresponds to a transition between crystal field split components of the ${}^4F_{3/2}$ and ${}^4I_{11/2}$ states. Other laser transitions are

$$\begin{aligned} {}^4F_{3/2} &\rightarrow {}^4I_{9/2} \quad \lambda = 946 \text{ nm} \\ {}^4F_{3/2} &\rightarrow {}^4I_{13/2} \quad = 1319 \\ {}^4F_{3/2} &\rightarrow {}^4I_{15/2} \quad = 1833 \end{aligned}$$

It is evident that these all correspond to transitions to excited states with energies that exceed thermal energies at 300 K. Hence, the Nd–YAG laser is a true four-level system. This implies that the threshold population inversion will be significantly smaller than that of the ruby laser which is a three-level system (compare Tables 1.3 and 1.1).

The relatively narrow linewidth of the 1064-nm line in Nd–YAG facilitates CW operation at room temperature. The result is that the CW Nd–YAG laser is second only to the CW CO_2 laser in terms of power generated. However, it does have a considerably lower overall efficiency (typically $<2\%$). Pumping of the Nd–YAG laser is usually with xenon of krypton arc lamps. Kryton lamps are well suited to Nd–YAG because their emission overlaps bands at $\sim$14,000–16,000 cm^{-1} of the Nd^{3+} ion (Figure 1.3).

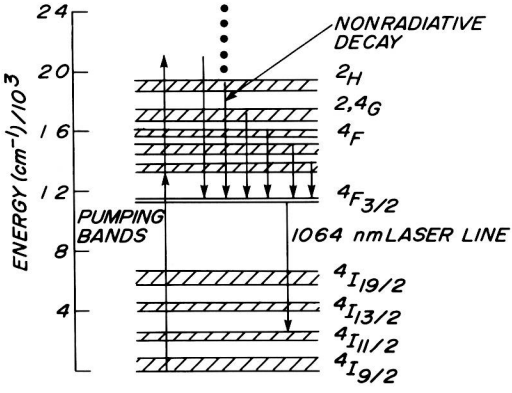

Figure 1.3. Energy levels in the Nd–YAG laser.