Photon-based Nanoscience and Nanobiotechnology

Edited by

Jan J. Dubowski and
Stoyan Tanev

NATO Science Series

II. Mathematics, Physics and Chemistry – Vol. 239

Photon-based Nanoscience and Nanobiotechnology

TB383-53
P575
2005

edited by

Jan J. Dubowski
Center of Excellence for Information Engineering,
Université de Sherbrooke, Sherbrooke, QC,
Canada

and

Stoyan Tanev
Carleton University, Ottawa, ON,
Canada

E2007001972

Springer

Published in cooperation with NATO Public Diplomacy Division

Proceedings of the NATO Advanced Study Institute on
Photon-based Nanoscience and Technology: from Atomic Level
Manipulation to Materials Synthesis and Nano-Biodevice Manufacturing
(Photon-NST'2005), Sherbrooke,
Quebec, Canada,
19–29 September 2005

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN-10 1-4020-5522-6 (PB)
ISBN-13 978-1-4020-5522-5 (PB)
ISBN-10 1-4020-5521-8 (HB)
ISBN-13 978-1-4020-5521-8 (HB)
ISBN-10 1-4020-5523-4 (e-book)
ISBN-13 978-1-4020-5523-2 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

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Series II: Mathematics, Physics and Chemistry – Vol. 239

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Preface

Jan J. DUBOWSKI
Center of Excellence for Information Engineering
Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada
and
Stoyan TANEV
Department of Systems and Computer Engineering
Faculty of Engineering and Design
Carleton University, Ottawa, Ontario K1S 5B6, Canada

The content of this book is based on peer reviewed invited articles corresponding to the tutorial presentations that were delivered in the frame of a NATO Advanced Study Institute (ASI) *'Photon-based Nanoscience and Technology: From Atomic Level Manipulation to Materials Synthesis and Nanobiodevice Manufacturing (Photon-NST'2005)'* held in Orford-Sherbrooke, Québec, Canada, September 19-29, 2005. The ASI was opened by John Polanyi, the 1986 Nobel Prize winner in chemistry, whose lecture on 'The Atomic Patterning of Surface by Chemical Reactions' set the stage for this frontier research and advanced technology forum.

Light has always played a significant role in the synthesis of materials and formation of small-scale solid structures. Until recently, the wavelength of photons has been the key factor limiting the minimum possible dimensions of two-dimensional or three-dimensional structures that they could produce. The invention of holographic and phase mask projection has enabled engineers to fabricate devices with characteristic features much smaller than the wavelength of the light used for processing. A further reduction of device dimensions has been achieved by implementing the processes that rely strongly on the non-linear effects of light-matter interaction. Photon-based nanoscience and technologies (Photon-NST) have created exciting opportunities and enabled new solutions with both documented and potential impact in such areas as communications, consumer electronics, automotive and aerospace industry. In addition, the accumulated to-date results of photon-based synthesis, deposition, etching, surface modification and particle manipulation demonstrate that the laser has the potential to offer enabling solutions for various needs of nano-scale processing, including fabrication and characterization of nano(bio)material devices and systems, and it is expected to significantly contribute to the development of Nanobiophotonics and Nanomedicine. The Photon-NST advancements have brought exciting nanoengineering tools for biomedical sciences, environmental monitoring, security and defense. The intention of this book was to provide the Reader, primarily graduate students and young researchers in materials engineering, bio(chem)physics, medical physics and biophysics, with a set of articles reviewing state-of-the art research and recent advancements in the field of photon-matter interaction for micro/nanomaterials synthesis and manipulation of properties of biological and inorganic materials at the atomic level.

An understanding of the physical and chemical aspects of the laser-matter interaction is very important for a deeper appreciation of the advances in photon-based nanoscience and technology. The chapter by Dickinson ('*Physical and chemical aspects...*') is a suitable reference addressing this problem. For a Reader specializing in the theory of laser-matter interactions, we recommend the chapter by Bandrauk et al. ('*Attosecond control of electrons...*'), which discuses the concept of an 'attosecond science'. The principles of nanoscale control of optical functions in solids and excited state dynamics of biomedical nanostructures are discussed by Prasad ('*Fundamentals of Nanobiophotonics*'), while Wilson presents an exhaustive review of the potential uses of nanoparticles in oncology, as well as a discussion of photonic-based techniques for both therapeutic and diagnostic applications ('*Photonic and non-photonics based nanoparticles...*'). A discussion of the definition of nanomedicine and the strategic Canadian initiative in the area of regenerative medicine is found in the chapter written by Marcotte and Quirion ('*A summary of Canadian nanomedicine research...*'). The application of the finite-difference time-domain modeling technique to study the effect of optical immersion based enhancing of phase microscope imaging of single and multiple gold nanoparticles in biological cells is discussed by Tanev et al. ('*Finite-difference time-domain modeling...*'). The fundamentals of plasmonics and the application of planar composite materials comprising metal nanocrystals for photonic sensor applications are discussed by Haglund ('*Nonlinear optical physics...*'). In another chapter ('*Applications of free-electron laser...*') Haglund discusses the status of current research concerning the use of the free-electron laser in medicine, biochemical analysis and organic thin-film deposition. A novel biosensor approach, based on the application of arrays of epitaxial quantum dots that have previously been known for their applications in advanced communication devices such as quantum dot lasers, is discussed by Dubowski ('*Quantum dot bio-template...*'). Laser synthesis of single-walled carbon nanotubes and nanohorns is discussed by Geohegan et al. ('*Laser-based synthesis...*') and Lippert ('*Molecular design of polymers...*') reviews the current status of designing polyimides and polymers dedicated for processing with lasers. Livingston and Helvajian ('*Photophysical properties that activate selective changes...*') investigate the fundamental effects of photoactivated changes in photostructurable glass ceramic materials and the application of this technology for manufacturing of so called 'nanosatellite class space vehicles'. The photostructurable glass has also been used for the fabrication of 3D microstructures of some lab-on-a-chip devices using a femtosecond laser technology. This field is reviewed in the chapter by Sugioka et al. ('*Three-dimensional micro and nanochips...*'). The design, operation, parametric monitoring and theory underlying the liquid phase photodeposition processes of nanosize colloid systems, such as a-Se, ZnS and Au, is discussed in the chapter by Peled and Mirchin ('*Photo-assisted processes...*') and the concept and results of using surface plasmon resonance for the fabrication of gold nanoparticles with a well-defined shape is discussed by Ouacha and Träger ('*Controlling the surface plasmon resonances...*').

This book is not to be read from the first to the last chapter but, rather, it has been intended as a reference to photon-based nanoscience and related technological problems concerning the growing field of nanobiophotonics. We hope that it will be of use not only to a young generation of researchers entering this field, but also to some of the seasoned scientists as well.

Acknowledgements

The editors are grateful to all supporting organizations and people that made this ASI possible. Our special thanks are directed towards the NATO Security through Science Program (Brussels, Belgium), US Air Force Office of Scientific Research, Canadian Institutes of Health Research, and Canadian Institute for Photonic Innovations. We thank Vitesse Re-Skilling™ Canada for partnering in setting the initial vision of the ASI and for providing the organizational infrastructure during the meeting; the Canadian Department of Foreign Affairs and its Global Partnership Program that together with the International Science and Technology Center in Moscow (Russia) supported the participation of Russian scientists; the Canadian International Development Agency that together with the Science and Technology Center in Kiev (Ukraine) supported the participation of Ukrainian scientists. We also thank the Holon Academic Institute of Technology (Israel), the State University of New York at Buffalo (USA) and the Université de Sherbrooke (Canada) for supporting the participation of their students in this event.

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PHYSICAL AND CHEMICAL ASPECTS OF LASER-MATERIALS INTERACTIONS

J.T. DICKINSON
Surface Dynamics Laboratory, Physics/Astronomy Department and Materials Science Program, Washington State University, Pullman, WA USA 99164-2814

Abstract. The use of lasers in to modify and characterize materials is an increasingly attractive choice for high technology manufacturing as well as analytical and medical applications. As we push for more demanding tasks and for smaller dimensions, an understanding of the underlying physical and chemical aspects of problems becomes important. Here we discuss some of these issues relevant to most applications involving laser materials interactions.

Keywords: laser processing of materials, physical and chemical properties, laser-materials interactions, micromachining

1. Introduction

Soon after the development of the first laser it was suggested that it would have uses as a manufacturing tool due to many of the advantages of radiation sources over conventional mechanical and thermal techniques. Furthermore, a number of biological and medical applications were considered such as surgery. Today, lasers are used for a number of laser processing tasks in advanced applications in industry. As the commercial boom in microelectronic and optoelectronic devices and the trend toward miniaturization continues, industrial use of lasers will play an increasingly important role. Materials ranging from ceramics/glasses, metals, semiconductors, polymers, natural and manmade fibers and composites have all been shown to interact with one or more laser types in useful ways. A number of biotechnical applications requiring precision and highly reproducible techniques rely heavily on laser processing. The arsenal of lasers of current or future interest includes both CW and pulsed lasers. The

J.J. Dubowski and S. Tanev (eds.), Photon-based Nanoscience and Nanobiotechnology, 1–30.
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commonly used lasers include the CO_2 laser, Excimer Lasers, Solid State Lasers (including diode pumped YAG and Ti:Sapphire lasers), Metal Vapor Lasers, and for some applications, Diode (semiconductor) lasers. The microfabrication and processing applications that are potentially well matched to using lasers include:

- etching
- cutting
- stripping
- cleaning
- drilling
- surface modification
- dry patterning
- scribing
- deposition (PLD)
- diagnostics
- trimming
- welding/soldering
- bonding
- marking/printing
- annealing
- photolithography
- mask fabrication
- 3D microstructures
- laser recrystallization.

Microhole drilling and trimming of components and laser recrystallization are certainly the most successful applications of lasers in microelectronics. The "advantages" of using lasers in processing and biomedical applications always must be weighed against disadvantages. A typical list of advantages of using lasers includes:

- close tolerance (resolution; feature size-usually wavelength dependent)
- repeatability (often excellent)
- zone of modification can be near-surface (i.e., for strong absorption) and in the bulk for transparent materials (using multiphoton absorption techniques)
- potential unit cost reductions, cost effectiveness
- material versatility (including fragile, ultrathin, highly reflective materials)
- roughness of Surfaces (Sometimes < nm)
- minimal distortion in heat affected zones

- no tooling to wear out or change over – no contact with surface
- non-contact processing eliminates unwanted stress on materials; contamination eliminated
- clean processing: minimal debris, burrs, uplifted recast
- flexibility - fast setups achieved with computer controls.

However, in evaluating these "advantages" one must weigh the extent or degree of each, thus the quotation marks around the word advantages. For example, is the resulting roughness tolerable, is a small amount of re-deposited particulates acceptable, is the process truly competitive with traditional methods cost-wise. Regarding costs, always lurking in the background are the expenses for operator training and addressing safety concerns. The "complaints" of a fabrication manager might include:

- it doesn't work (it breaks it, instead of makes it)
- it's unpredictable (e.g., no software package to model the entire process)
- it's too slow
- it's too big (the modified area) or
- it's too small
- it's only one at a time
- it messes up (harms, degrades, contaminates) the 'neighborhood'
- it's too expensive
- it's only line of sight
- the laser and/or optics need too much maintenance.

Basic physics and chemistry can help address only a few of these issues. Of course, we note that the university academics state in every research proposal they submit: "*We need to understand the underlying mechanisms so that we can advance the technology*." In truth, most of the advancements in fabrication and processing are occurring ahead of the science and can't wait. The same is true in biomedical applications. It is often only when a particular process is very promising yet is not quite working, or not optimized, or has too many uncontrolled parameters that fundamental understanding would be a benefit. If the value-added by performing some manufacturing or biomedical step using lasers is high, this further motivates more basic research on mechanisms and understanding. In general, we want to understand the physical processes accompanying laser interactions with matter under conditions typical for laser-materials modification, removal, etching, etc. We certainly need to explore the relevant interactions of laser beams interaction with metals, dielectrics, semiconductors, polymers and biological tissue. Such physical processes as heat transfer, phase transitions, material removal, plasma formation, and synthesis of nanoclusters and nanocrystalline films are very important.

2. Physical and Chemical Aspects

So let us explore a few of the major questions and issues involved in laser materials interactions, particularly those that involve material removal and heat driven processes. Some of the important aspects (much more than we can discuss) of laser materials interactions are as follows:

- light absorption processes (linear; nonlinear – multiphoton, multiple-photon; defects)
- absorbed energy density vs. position and time
- emission mechanisms (e-, ions, neutrals, clusters, "chunks")
- factors influencing rates of material removal and/or material modification
- photothermal vs. photoelectronic (fs, ps, ns)
- role of thermal-mechanical phenomena (∇T, shock) including
  - melting/Resolidification
  - fracture, spallation (particles)
  - diffusion or segregation
  - vaporization
  - condensation of vapors in gas phase (particles)
- role of external environment (reactive gases, liquids, pressure)
- equilibrium thermodynamics vs. non-equilibrium
- role of laser-plume interactions
- role of laser parameters (λ, t_{pulse}, I_{peak}, θ, spot size, rep. Rate, no. of pulses)
- understanding dependence on target parameters (e.g., optical & thermal properties, defects, morphology, spatial distributions, interfaces)
- generating predictive models (grand challenge to theorists)

All of these facets are addressable with today's knowledge and understanding of the underlying physics and chemistry. We want to emphasize that much of what is happening in the use of lasers involves either bond breaking or bond making. Usually it is desired to do this locally (precisely), quickly (to be cost effective; to avoid too much heating), and with "no" collateral damage. The use of lasers in fabrication is similar to the use of lasers in medicine – just like the medical doctor, the fabricator must abide by the constraint: "*Above All, Do No Harm*". Minimizing this surrounding "damage" is often the biggest challenge.

2.1. BASIC BOND BREAKING

Often the types of bonds being broken (or made) influences the choice of laser parameters which include wavelength, pulse width/CW, peak irradiance, angle of incidence, spot size, repetition rate, and number of pulses. We usually consider four fundamental types of bonding:

- covalent bonding (diamond, Si, Ge, GaAs, GaN, BN, SiO_2)
- ionic bonding (alkali halides, alkaline earth halides, metal oxides such as MgO)
- metallic bonding (metals in general)
- intermolecular forces (Hydrogen Bonding - strongest)
- dipole-dipole forces
- London dispersion forces (non-polar structures interacting - weakest).

An example of where intermolecular forces would be important are interfaces which will be (making bonds) or are (breaking bonds)connected via adhesive bonds; another example is the entire range of interactions involving unwanted 'pesky' particles adhering to substrates which need to be removed. Using laser cleaning to remove a particle thus requires that these intermolecular forces be overcome in order to detach the particle. Electrostatic charge, if present, can of course increase the bonding of particles to surfaces considerably. The use of water ("steam cleaning") in laser cleaning would assist in neutralizing this charge along with the advantages of nucleating bubbles to assist lifting particles.[1-3] Of course all glassy polymers consist of covalently bonded polymer chains with intermolecular forces interacting between the chains. Thus, the properties of common polymers, such as polymethylmetha-crylate (PMMA), polycarbonate (PC), and polystyrene (PS), are strongly dependent on these intermolecular forces. These lead to inter-chain friction, entanglements, and free-volume dependent attributes (e.g., thermal properties; gas diffusivity).

Figure 1 shows schematically the interaction of a laser beam with a structure of some complexity. Assuming a reasonable degree of absorption (so we can ignore transmission), the incident photons are absorbed either due to excitation of electrons or for longer wavelengths, excitation of vibrational modes. The reflectivity of the material then dictates how much of the incident beam is absorbed. The 3D distribution of absorption centers exposed to the incident beam and their optical properties in relation to the laser light dictate the energy density distribution in the near surface region. In metals, absorption takes place very near the surface and can occur by excitation of both conduction band (free electron-like) and valance band (interband absorption) electrons are the absorbing entities. These electrons transfer their increased kinetic energy to the lattice via phonon scattering on time scales of ps, resulting in a temperature increase. For long pulses (> ps) heating is occurring during the pulse and so in general one can treat light energy to heat in one step.

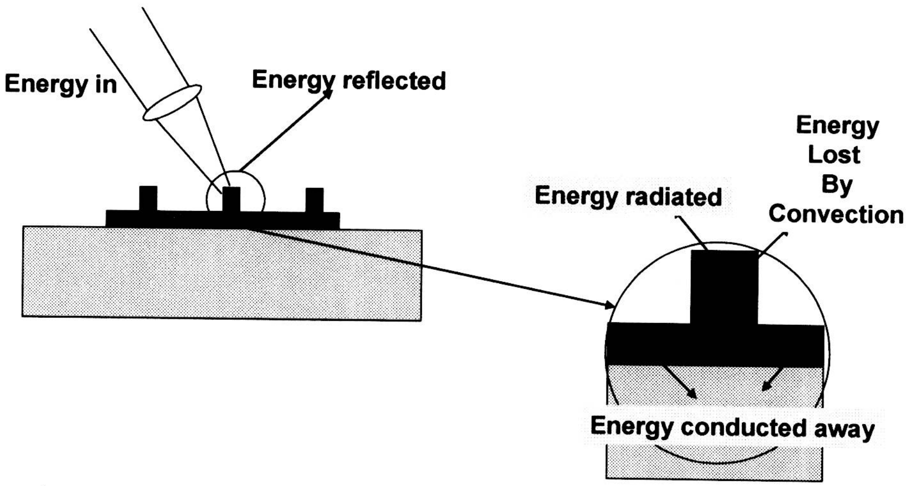

Figure 1. Schematic of relevant interactions and consequences of energy absorption.

For semiconductors and insulators, absorption is either through vibrational excitation (requiring infrared light matching allowed vibrational transitions of the material) or electronic excitations (e.g., via chromophores, defects, or band-to-band transitions). The electronic energy tends to be more localized than in metals, but in "real materials", the electronic energy is again quickly transformed into thermal energy. Atomic dimension energy localization can assist in the breakdown of materials, particularly in crystalline ceramics and silica-based glasses. For example, electron-hole pairs in an insulator are trapped at a lattice site which then may lead to motion of nuclei – the beginnings of decomposition of the material, all non-thermal in nature. Numerous examples of such phenomena are presented in the book by Itoh and Stoneham.[4] However, many of the rates of material removal using lasers, even those initiated by electronic processes, are still thermally enhanced or thermally controlled; thus, in general, the practical use of lasers in fabrication is dominated by thermal processes--thus arguing over "photoelectronic" vs. "photothermal" is moot.

2.2. COMMENTS ON THERMAL MODELING

In seeking precision in processing, the fate of this deposited energy is highly significant. As seen in Fig. 1, the dispersion of the thermal energy away from the region where it was absorbed can involve radiative, convective, and conductive transport. By far the most important for practical applications is the heat transport by diffusion/conduction away from the higher temperature irradiated region into the cooler surrounding material. The rates and dimensions involved determine the spatial region that reaches high temperatures - the so-called Heat Affected Zone. Many modeling efforts have been focused on predicting the spatial and temporal distribution, T(**r**,t), during and following the laser pulse.[5] One can readily write down the appropriate time and space dependent heat conduction equation:

$$\rho C_p \frac{\partial T(\mathbf{r},t)}{\partial t} = \frac{H}{C_p} + \nabla \bullet [\kappa(\mathbf{r},T)\nabla T(\mathbf{r},t)]$$

where $k \equiv \rho C_p \kappa$ is the thermal conductivity with units of Joules and k is the thermal conductivity (with units of Joule/(mKs), κ is thermal diffusivity in m^2/s, H is the Heat Input per unit mass in Joule/(Kg.s)* $\alpha I(\boldsymbol{r},t)$ (linear absorption), α is the absorption coefficient, I is the instantaneous power density of laser radiation. Note that many of these "constants" are actually temperature dependent and must be treated as such.

The methods commonly used to solve the heat conduction equation analytically or numerically are:

Laplace transforms Green's functions Fourier transforms	Analytic
Stochastic/Monte Carlo Finite Differences	Numerical

Computer models suffer from two potential difficulties:

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