edited by

Ion N. Mihailescu | Anna Paola Caricato

## Pulsed Laser Ablation

Advances and Applications in Nanoparticles and Nanostructuring Thin Films



Pulsed laser-based techniques for depositing and processing materials are an important area of modern experimental and theoretical scientific research and development, with promising, challenging opportunities in the fields of nanofabrication and nanostructuring. An understanding of the interplay between deposition/processing conditions, laser parameters, and material properties and dimensionality is required for improved fundamental knowledge and novel applications.

This book discusses the basic principles of pulsed laser–matter interaction, with a focus on its peculiarities and perspectives compared to other conventional techniques and state-of-the-art applications. The book starts with an overview of growth topics, followed by a discussion of laser–matter interaction based on laser pulse duration, background conditions, materials, and combinations of materials and structures. This information outlines a foundation for introducing examples of laser nanostructuring/processing of materials, pointing out the importance of pulsed laser–based technologies in modern (nano)science.

Compared to similar texts and monographs, the book offers a comprehensive review that includes bottom-up and top-down laser-induced processes for nanoparticle and nanomicrostructure generation. Theoretical models are discussed by correlation with advanced experimental protocols in order to account for the fundamentals and underline physical mechanisms of laser-matter interaction. Reputed, internationally recognized experts in the laser-based deposition and processing field have contributed to this book. Each chapter treats a specific topic in a simple and self-explanatory way, including both fundamentals and examples from the contributors' research that introduce the reader to the field at each level (theory and practice). The book serves as an introduction to the field and as a foundation for further specific readings for graduate and postgraduate students of physics, chemistry, materials science, and engineering and researchers in laser materials processing, who will gain physical insight into and advanced knowledge of the mechanisms and processes involved in any deposition/processing experiment based on pulsed laser-matter interaction.



**Ion N. Mihailescu** is university professor and senior scientific researcher (1st degree) at the National Institute for Lasers, Plasma and Radiation Physics, Romania (www.inflpr.ro). He has a large experience in laser interactions, lasers and plasma physics, nanostructured thin-film technology, nanopowder generation and characterization, surface physics and engineering, laser spectroscopy, and materials processing by advanced laser technologies. He has authored 441

publications, 195 scientific papers published in proceedings of international conferences, and 20 books and monographs and holds 12 patents. He has an h-index of 36 and an i10-index of 181 (http://www.researcherid.com/rid/A-5403-2011). He is the first recipient (1994) of the Galileo Galilei award for "outstanding contribution in the field of optics" and has also received the Doctor Honoris Causa of Université Cergy-Pontoise, France (2015).



Anna Paola Caricato is a professor at the Department of Mathematics and Physics "E. De Giorgi" of the University of Salento, Italy. She received her PhD in physics from the University of Modena and Reggio Emilia, Italy, in 2000. Her research focuses on (i) laser–matter interaction for the deposition of thin films and nanoparticles by laser ablation for applications in sensors, optoelectronic devices, and solar cells and (ii) matrix-assisted pulsed laser evaporation for the deposition of organic

ISBN 978-981-4774-23-9

films, polymer multilayers, nanomaterials, and composite films. She has authored more than 120 publications in peer-reviewed international journals and 6 book chapters and holds 2 patents. She has also served as a conference co-chair and committee member for international conferences in laser-matter interactions and applications.





## Pulsed Laser Ablation

# Advances and Applications in Nanoparticles and Nanostructuring Thin Films

edited by
Ion N. Mihailescu
Anna Paola Caricato

#### Published by

Pan Stanford Publishing Pte. Ltd. Penthouse Level, Suntec Tower 3 8 Temasek Boulevard Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

#### **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

## Pulsed Laser Ablation: Advances and Applications in Nanoparticles and Nanostructuring Thin Films

Copyright © 2018 by Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4774-23-9 (Hardcover) ISBN 978-1-315-18523-1 (eBook)

# Pulsed Laser Ablation



#### **Preface**

Nanotechnology and nanomaterials are at the origin of major progress, breakthroughs, and solutions to a vast number of engineering, biology, and medicine challenges. In fact, at the nanoscale, and at a macroscopic scale as well, the onset of size-dependent phenomena occurs and matter begins to exhibit entirely new properties. The advantage connected to the small feature size of nanostructured materials is exploited in many different applications, both in ordinary life and in high-technology fields.

Obviously, the possibility to valorize the new properties of nanomaterials is strictly connected to the availability of manufacturing processes and characterization techniques.

Among manufacturing methods, pulsed laser-based techniques offer several advantages compared to "traditional" ones for the fabrication of nanomaterials and surface nanostructures, due to the possibility to tune many independent processing parameters. Laser and laser ablation proved important and prospective in various fields, spanning from a better understanding of fundamental physical mechanisms and light-matter interactions to a large range of applications in physics, chemistry, biology, medicine, materials science, manufacturing technology, and even arts and conservation.

This book consists of 14 chapters covering a broad range of topics, written by internationally recognized experts in the field, on the recent advances in the application of laser ablation for the generation of nanoparticles and surface nano- and microstructures and their applications.

It includes a comprehensive overview of the classical theory of growth, with a focus on the importance of kinetic factors and processes in far-from-equilibrium deposition techniques such as pulsed laser deposition (Chapter 1). The wetting, adherence, and nanostructuring properties of the synthesized coatings, by pulsed laser processes, are described and discussed in Chapter 7. A detailed description of the mechanisms and significance of deposition parameters on nanoparticle immobilization and production in

different environments (e.g., vacuum, Chapter 2; a high-gas-pressure atmosphere, Chapter 3; liquid, Chapter 5; and matrices, Chapter 6), pulse duration (i.e., the ns regime, Chapters 2, 3, and 5; or the fs regime, Chapters 4 and 5), and use of two time-delayed laser pulses (Chapter 9) is provided. An overview of the results obtained in recent molecular dynamic simulations of laser ablation of metal targets in vacuum, a background gas, and a liquid environment (Chapter 12) is also given.

The processing of materials by fs laser pulses has attracted a great deal of attention because fs pulse energy can be precisely and rapidly delivered to the material without detectable heat perturbation of the neighboring zones. In some cases, periodic micro- and nanostructures can be generated directly (without the use of masks or chemical photoresists to relieve the environmental concerns) in almost any samples from semiconductor to dielectric materials and polymers, supplying relevant results to be used in different applications like nanofluidics, nanophotonics, and biomedical devices.

The effects of some key parameters, including multiple pulses, variable pulse shaping, and fluence, which could be useful in the laser nanostructuring of surfaces and micromachining of different materials (e.g., dielectric, Chapter 10; semiconductor, Chapter 11; and polymer, Chapter 13), are reviewed and discussed from fundamental and/or applicative points of view. The use of laser-based material processing techniques, such as pulsed laser deposition (PLD), laserinduced forward transfer (LIFT), material processing via 3D laser structuring (LS), and laser annealing (LA) techniques for energy storage applications is analyzed in Chapter 14.

Next, Chapter 8 is devoted to the importance of the use of core-shell nanoparticles when different material properties must be merged at the nanoscale to meet the requirements for smart applications.

In the opinion of the authors, the book offers a comprehensive review of the latest advances in top research and development in the laser material processing field for nanoparticles and nanomicrostructure generation and exploitation of different kinds of materials. Theoretical models are discussed by correlation with advanced experimental protocols, to explain the fundamentals and underline physical mechanisms of laser-matter interaction.

The book was conceived as a starting point and guide for students and young researchers who are beginning to initiate in the field of nanostructures and nanoparticles.

Last but not least, the two editors would like to thank all of the chapter contributors for their great efforts and kind cooperation in preparing this book.

Ion N. Mihailescu and Anna Paola Caricato

2018

### Contents

Prefa	исе			xiii	
1.	Surface	e Energy	and Nucleation Modes	1	
	Maura Cesaria				
	1.1	Introd	uction	2	
	1.2		Thermodynamic Background Concepts		
		1.2.1	Thermodynamic Potentials and Surface		
			Free Energy	5	
		1.2.2	Phase Transformations of a		
			Thermodynamic System and		
			Supersaturation	8	
		1.2.3	Strain and Epitaxial Growth	9	
	1.3	Therm	odynamic Nucleation Theory and Growth		
		Modes		13	
		1.3.1	Principles of Nucleation Theory	14	
		1.3.2	Growth Modes at Thermodynamic		
			Equilibrium	20	
	1.4	Elementary Kinetic Processes on Surfaces and			
		the En	ergy Landscape	25	
		1.4.1	Adsorption, Real Substrates, and		
			Surface Elementary Processes	26	
		1.4.2	Characteristic Kinetic Coefficients,		
			Energy Barriers, and Timescales	30	
	1.5	Conde	nsation Processes and Kinetic-Driven		
		Growtl	h Modes	34	
		1.5.1	Kinetic Control of Nucleation	35	
		1.5.2	Intralayer and Interlayer Diffusion,		
			Island Coalescence, and Growth Modes	37	
		1.5.3	Microstructure Evolution	42	
	1.6 Deposition Techniques in Nanoscience and				
		Advantages of the Pulsed Laser Approaches			
	1.7	Growt	h Opportunities by the PLD Technique	50	
		1.7.1	Distinctive Characteristics of the PLD		
			Approach	51	

		1.7.2	Growth Manipulations by PLD	59			
	1.8	Conclu	usions	68			
2.	Nanos	econd L	aser Ablation and Processing of Solid				
	Targets	s in Vacu	uum or in a Low-Gas Atmosphere	85			
	Vincenzo Resta, Ramón J. Peláez, and						
	Anna Paola Caricato						
	2.1 Introduction						
	2.2	Plasma	Plasma Dynamics and Expansion				
		2.2.1	Plasma Parameters: Temperature				
			and Density	91			
		2.2.2	Plasma Composition: Atom and Ion				
			Distribution/Yields	93			
	2.3		ction of Metal Nanoparticles by Pulsed				
		Laser	Deposition	100			
		2.3.1	Dependence with the Number of				
			Laser Pulses in the Metal Target	101			
		2.3.2	Dependence with the Laser Fluence	106			
		2.3.3					
			Deposition in Nanoparticle Formation				
			and Dependence with the Substrate	110			
	2.4	Therm	nal Process	113			
		2.4.1	Substrate Temperatures	113			
		2.4.2	Postheating by Laser Irradiation	115			
3.	Nanos	econd L	aser Ablation of Solid Targets in a				
	High-Pressure Atmosphere			131			
	Sebast	iano Tri	usso, Fortunato Neri, and				
	Paolo Maria Ossi						
	3.1	Introd	uction	132			
	3.2	Compa	arison between Some Basics of Laser				
		Ablati	on in Vacuum and in a Gas at High				
		Pressu	ire	133			
	3.3	Nanop	particle Synthesis and Assembling				
		upon A	Ablation in a High-Pressure Gas:				
		Selecte	ed Examples	136			
	3.4	Depos	ition of Noble Metal Nanoparticle				
		Arrays	s for Application in Biomedical Sensing	142			
	3.5	Conclu	isions	150			

4.	Femtosecond Laser Ablation of Solid Targets in Vacuum and Low-Pressure Gas Atmosphere 155					
	Vacuum and Low-Pressure Gas Atmosphere Salvatore Amoruso					
	4.1	Introd		156		
	4.2	-	mental and Theoretical Analyses of			
	4.0		rly Stage of Femtosecond Laser Ablation	161		
	4.3		mental Analysis of Late Stages of			
		Femtosecond Laser Ablation and Plume Propagation				
				167		
		4.3.1	High-Vacuum Expansion	168		
		4.3.2	Propagation in a Low-Pressure	174		
	4.4	Foresto	Background Gas	174		
	4.4		second Laser Ablation of Thin Films	179		
	4.5					
	4.6	Films .6 Conclusions				
	4.0	Concid	ISIOIIS	182		
5.	Short-Pulse Laser Near-Field Ablation of Solid Targets					
	under Liquids			193		
	M. Ulmeanu, P. Petkov, F. Jipa, E. Brousseau, and					
	M. N. R. Ashfold					
	5.1	Introduction				
	5.2	Introduction Working Principle of the LILAC Lithography				
		5.2.1	Preparing the Si Substrates	195 196		
		5.2.2	Preparing the Colloidal Mask	197		
		5.2.3	Laser Processing Parameters	198		
		5.2.4	Focusing the Laser Beam through the			
			Liquids	198		
		5.2.5	Finite-Difference Time Domain			
			Simulations	200		
	5.3	Experi	mental Demonstrations	202		
	5.4	Conclu	asions	204		
6.	MAPIF	Denosi	tion of Nanomaterials	207		
	Enikö György and Anna Paola Caricato					
	6.2	Introduction 208 Ultraviolet Matrix-Assisted Pulsed Laser				
	0.2	Evapor		215		
		Lvapol	iativii	413		

	6.3	Infrare	ed Matrix-	Assisted Pulsed Laser			
		Evapor	ration		230		
	6.4	Invers	e Matrix- <i>A</i>	Assisted Pulsed Laser			
		Evapor	ration		234		
	6.5	Conclu	isions		236		
7	. Thin Films and Nanoparticles by Pulsed Laser						
•				herence, and Nanostructuring	245		
				n N. Mihailescu	243		
	7.1	Introd		· · · · · · · · · · · · · · · · · · ·	246		
	7.2	Wettin			248		
	7.2	7.2.1	Definitio	ons	248		
		7.2.2			251		
	7.3	Adhere		mples	254		
	7.5	7.3.1		echanisms	254		
		7.3.2		ations and Examples	255		
	7.4		tructuring	-	258		
	/.1	7.4.1		-	258		
		7.4.2		of Nanostructures	259		
		7.1.2	7.4.2.1	Conventional imaging	259		
			7.4.2.2	0 0	20)		
			7111212	intensity imaging	260		
		7.4.3	Nanostr	ucturing with Advanced PLD	200		
		, , , , , ,	Techniq		262		
		7.4.4	Applicat		265		
			7.4.4.1		265		
			7.4.4.2	9	266		
			7.4.4.3	Nanoparticles for SERS	267		
	7.5	Conclu	isions	P	268		
Q	Coro-S	hall Nar	oparticle	s for Enorgy Storago Applications	277		
٥.	Core-Shell Nanoparticles for Energy Storage Applications 277						
	Manish Kothakonda, Briley Bourgeois, Brian C. Riggs,						
	Venkata Sreenivas Puli, Ravinder Elupula, Muhammad Ejaz, Shiva Adireddy, Scott M. Grayson,						
		-	. Chrisey	Autready, Scott M. Grayson,			
		•	-		0.70		
	8.1	Introd			278		
		8.1.1	_	rticle Property Selection	280		
		8.1.2		rticle Synthesis	281		
			8.1.2.1	Core-shell nanoparticles			
				prepared by the grafting-from	281		
				TOTAL	/ X I		

			8.1.2.2	Core-shell nanoparticles		
				prepared by the grafting-to		
				route	283	
	8.2	Experi	mental Se	ection	286	
		8.2.1		rticle Synthesis	286	
		8.2.2	-	rticles Synthesis by Pulsed		
			Laser Ab		288	
		8.2.3		is of BaTiO <sub>3</sub> Nanoparticles		
				olvothermal Method	289	
		8.2.4		rization of Nanoparticles	292	
			8.2.4.1	Synthesis of PGMA-BaTiO <sub>3</sub>		
				core-shell nanostructures		
				by grafting-from	292	
			8.2.4.2			
				GMA-BaTiO <sub>3</sub> core-shell		
				nanostructures by grafting-to	294	
	8.3	Materi	als Chara	cterization	295	
	8.4	Experimental Observation			296	
		8.4.1		ic Properties and Leakage		
				Behavior	299	
	8.5	Conclu	isions		303	
9.	Nanoparticle Generation by Double-Pulse Laser					
	Ablatio				317	
	Emanuel Axente, Tatiana E. Itina, and Jörg Hermann					
	9.1	Introduction				
	9.2	Typical Experimental Design for Laser-Matter				
		Interactions with Double Pulses				
		9.2.1	Collinea	r Double-Pulse Interaction		
			Geometr	У	322	
		9.2.2	Orthogo	nal Double-Pulse Interaction		
			Geometi	У	322	
		9.2.3		ent for NP Generation with		
			Delayed	Short Laser Pulses	323	
	9.3	Investigation of Nanoparticles Produced by				
			Double-Pu	ılse Laser Ablation of Metals	325	
		9.3.1	Correlat	ion between Ablation		
			Efficience	cy and Nanoparticle Generation		
			in the Si	ngle-Pulse Regime	326	
		9.3.2	Influenc	e of Interpulse Delay on		
			Plume C	omposition	327	

		9.3.3	influence of interpulse Delay on	
			Ablation Depth and Crater Morphology	331
		9.3.4	Overview of Other Investigations in the	
			Field of Double-Pulse Laser–Matter	
			Interactions	334
	9.4	Modeli	ng of Double-Pulse Laser Ablation	338
		9.4.1	Fundamentals of Laser–Matter	
			Interactions	338
		9.4.2	Numerical Simulations of Short	
			Double-Pulse Interaction with Materials	341
	9.5	Conclu	sions and Perspectives	343
10.	Ultrafa	st Laser-	Induced Phenomena inside Transparent	
	Materi	als		357
	Felix Si	ma, Jian	a Xu, and Koji Sugioka	
	10.1	Introdu	uction	358
	10.2	Charac	teristics of Glass Material Processing	
		by Ultr	afast Laser Pulses	359
		10.2.1	Interaction Mechanism of Ultrafast	
			Laser Pulses with Glasses	359
			10.2.1.1 Nonlinear multiphoton	
			absorption	359
			10.2.1.2 Heat accumulation effects	362
		10.2.2	Spatial Resolution in Ultrafast Laser	
			Processing of Glass	363
	10.3		ormative Processing: ULP-Induced	
			al Modifications	366
	10.4		ctive Processing: Formation of 3D	
			and Nanofluidic Structure	370
		10.4.1	Ultrafast Laser-Induced Modification	
		10.10	Followed by Selective Wet Etching	370
			Liquid-Assisted ULP Processing	374
		10.4.3	Pros and Cons of the ULP 3D	075
	105	A 1 1	Subtractive Process	375
	10.5		ve Processing: ULP-Induced	276
			oolymerization of Photoresists	376
			Mechanisms and Limitations	376
		10.5.2	Applications of Two-Photon	270
	10.6	Urrhad J	Polymerization	379
	10.6	пургіа	ULP 3D Processing	381