Chapter 1
Introduction and Scope of the Book

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Abstract This chapter introduces the scope of the book. It is intended to guide the reader through the book, to find specific information by shortly summarizing information from the following chapters and to build a cross reference to the various applied methods and the corresponding applications. The laser as a powerful light source can be found in nearly any technical application, ranging from consumer electronics (CD, DVD, blu-ray player, scanner), metrology (including environmental monitoring), scientific research (laser development to novel fields in quantum physics, photonics and medicine), arts, industry, information technology to lithography and material processing. It is obvious that the laser meets many requirements from technical challenges inspired by natural evolutionary solutions. Not all of them can be treated in a single book, but a cross section of the powerful combination of both, laser technology and biomimetic thinking, form a powerful approach to novel technical application scenarios as presented in the next chapters, which are considered as guideline and orientation for the reader depending on a laser or application based approach.

1.1 Biomimetics as Inspiration for Laser-Based Methods and Applications

The term “biomimetics” commonly defines the understanding of natural structures and functions of biological systems and the corresponding translation of the observed working principles as models for the development of technical systems with enhanced

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properties. On one hand, nature takes advantage of structural features for tailoring and enhancing intrinsic material properties. These structures have been optimized during a long term of evolution. Prominent examples are e.g. structural colors [1], or the wetting behavior of a textured surface [2]. These examples are interesting for many technical applications in design, construction, architecture, robotics, energy management and surface engineering. Here, medical applications are biological lightweight construction and medical implants with biocompatible coatings.

On the other hand, direct processing of natural materials and substituting it by artificial biomaterials that mimic natural tissue are further aspects of learning from nature. By studying mechanisms of cell behavior as well as cell tissue interaction and designing adequate cell environments new aspects are introduced into tissue engineering.

1.1.1 Laser Sources

Without the invention of the laser and the unique properties of laser radiation many processes and innovations would not have been possible. Laser technology has experienced a strong development since its first demonstration in the 1960s. Today many different laser types and technical applications for laser radiation are state-of-the-art and new ones are about to be discovered. This short introduction summarizes the main features and concepts of laser processing and surveys the most important application scenarios of the laser as a versatile processing tool, which is presented in the context of biomimetics in the subsequent chapters of this book.

Nature provides many examples how evolution solved environmental issue for the purpose of survival of an organism. Hence, there are many technical problems that can look for inspiration within the framework of biomimetics. The application of laser technology in material science is comparably multifaceted. First of all there are many different laser sources available that are potentially matching a certain application. Secondly, the laser processing is in principle not limited to a certain class of materials. Basically most of known materials show modifications when processed by laser radiation. Consequently applications that are both, inspired by nature and involving laser technology are quite overlapping and a systematic approach to this topic can be quite different.

The selection of an appropriate laser for an envisaged application is mainly determined by the technical specifications of the laser such as wavelength, operational mode, power etc. The wavelength for material processing is demanded by the optical properties of the target material. The wavelength of the laser subsequently determines properties of the optical setup regarding the beam delivery with all included optomechanical components. The operational mode (continuous wave-cw or pulsed) directly influences the interaction regime with the target material and which paths of energy deposition can be triggered by the incident laser power.

Industrial applications are more demanding than scientific applications in terms of acquisition and operational costs, reliability of the laser sources, maintenance requirements, handling, ease of operation, technical complexity, and automation. These factors have great impact on the market value and prize of the final products. Some laser sources have gained specific importance and have made the way from pure research in laboratories to industrial fabrication and applications in material processing (cf. also Table 1.1). The laser types involved in the biomimetic applications and processes described in this book are shortly summarized in the next paragraphs.

1.1.1.1 CO_2 Lasers

The CO_2 laser is a gas laser and is one of the most important lasers in industrial applications regarding high power material processing such as machining, welding, cutting, drilling, and engraving. Although most metals reflect very well its radiation, the processing of metallic workpieces with such lasers is very common. CO_2 laser systems are available as pulsed or cw operating systems. Beam power up to 100 kW in cw operation is possible at rather high energy conversion factor (up to 30 %). The CO_2 laser represents currently the highest available cw power at reasonable costs and emits radiation at mid-infrared wavelength (10.6 μm). Low power systems are used in research and medicine. Medical applications are motivated by the good absorption of the laser wavelength in water and water containing tissue. The wavelength of the laser requires special optics (ZnSe as lens or window material, Cu as mirror) and cannot be passed through glass fibers, which is sometimes a drawback with respect to beam delivery.

With respect to biomimetics and the presented manufacturing methods, CO_2 lasers are used for selective laser sintering (see Chap. 4).

1.1.1.2 Excimer Lasers

Laser light sources in the ultraviolet spectral range are either frequency multiplied solid-state lasers or gas lasers. Especially excimer lasers provide pulsed high power ultraviolet to deep ultraviolet emission at a typical repetition rate of a few hundred Hz up to some kHz. The main scientific and industrial applications of excimer lasers are material processing, lithography and medicine, involving methods such as laser ablation, engraving, marking, surface and sub-surface modifications and coatings made via pulsed laser deposition in either projection or direct exposure mode. In projection mode, the laser light is projected via a mask onto a target for UV exposure. In direct exposure mode, the focused laser light directly ablates the material by moving the focused laser across the target. In projection mode the effect of the laser results either in patterned material removal or in exposure of the material without removal, which depends mainly on the laser fluence and applied pulse number.

The active medium of an excimer laser is a gas of electrically excited dimers (“excimer”, or more precisely excited complexes), where an excited noble gas atom and a halogen form a noble gas halide, which decays after a short time (typically

Table 1.1 Important laser types, emission characteristics and field of application

Lasertype	Gain medium	Emission characteristics (mode of operation, wavelengths, power/pulse energy)	Application
Ar-ion laser	Gas	cw(*) operation $\lambda = 488\,nm$, 514.5 nm some Watt	Spectroscopy, holography, machining
He-Ne laser	Gas	cw operation $\lambda = 633\,nm$ some 0.1 Watt	Alignment, spectroscopy, holography, Interferometry
He-Cd laser	Gas	cw operation $\lambda = 325\,nm$ some 10 mW	Lithography interferometry
Excimer laser	Gas	pulsed operation (ns) $\lambda = 157\,nm$ (F_2), 193 nm (ArF), 248 nm (KrF), 308 nm (XeCl) some Joule	Lithography, ablation, machining, surgery
CO_2 laser	Gas	cw, pulsed operation (µs) $\lambda = 10.6\,\mu m$ some mW to some kW	Machining, cutting, welding, drilling
Nd:YAG	Solid state	cw, pulsed operation (ns, ps) $\lambda = 1064\,nm$, 532 nm (SH**), 355 nm (TH), 266 nm (FH) some kW	Material processing, laser pumping, research, surgery
Ti:Sapphire	Solid state	pulsed operation (ps, fs) $\lambda = 670 - 1080\,nm$ some mJ	Spectroscopy, non-linear material processing
Nd:Glass	Solid state	pulsed operation (ms, ns, ps) $\lambda = 1062\,nm$ some 100 J	High energy multiple beam systems, laser fusion
AlGaAs	Semiconductor	cw, pulsed operation (µs) $\lambda = 780 - 880\,nm$ some kW (laser diode bars)	Machining, medical, optical discs, laser pumping
AlGaInP	Semiconductor	cw operation $\lambda = 630 - 680\,nm$	Machining, medical, optical discs, laser pumping
InGaAsP	Semiconductor	cw, pulsed operation (ps) $\lambda = 1150 - 1650\,nm$	Machining, medical, optical discs, laser pumping
GaN	Semiconductor	cw operation $\lambda = 405\,nm$	Optical discs, lithography
Dye laser	Dye	cw, pulsed operation (ns) $\lambda = 300 - 1200\,nm$, depends on used dye	Spectroscopy, research, medical

(*) cw = continuous wave, (**) SH = second harmonic, TH = third harmonic, FH = fourth harmonic. Adapted from [3] some ns) into the dissociated state (e.g. Kr*F → Kr + F) under emission of UV light. The type of excimer determines the wavelength of the emission. The technically most relevant excimers are ArF, KrF, XeCl, and XeF and there are manifold applications for excimer laser processes such as excimer based optical lithography [4], excimer laser chemical vapour deposition [5], excimer laser micromachining [6] or eye surgery [7]. The high photon energy of the excimer radiation is capable of directly breaking intramolecular bonds of the target material, without only negligible thermal impact on the surrounding material.

1.1.1.3 Nd:YAG, Nd:YLF, Nd:Glass Lasers

These solid state lasers provide high power radiation (some kW) with a fundamental wavelength in the near-infrared spectral range (e.g. fundamental wavelength of Nd:YAG laser: 1064 nm). The Nd doped laser crystal is commonly pumped by IR laser diodes (diode pumped solid state laser–DPSSL). Depending on the geometrical shape of the laser crystal, such lasers are often denoted as disc, rod or fiber lasers. Applications for these lasers are machining, medicine or pumping of other lasers such as Ti:Sapphire lasers for the generation of ultrashort pulses. These solid state lasers are use instead of CO_2 laser in sintering of metallic and ceramic materials as described in Chap. 4. By using higher harmonics of the emitted radiation, these lasers may substitute excimer lasers in the UV region for laser assisted deposition methods such as matrix assisted pulsed laser evaporation (Chap. 5), pulsed laser deposition (Chap. 7) or laser induced forward transfer (Chap. 8).

1.1.1.4 Ti:Sapphire Lasers

The active medium is a titanium doped Al_2O_3 crystal (Ti:Sapphire). This crystal emits in the near-infrared spectral region and shows a spectrally broad emission. Because of the uncertainty principle, a short light pulse consists of many spectral components and the active laser must support the stimulated emission for many longitudinal modes of the laser resonator. Hence, Ti:Sapphire laser are very well suited for the generation of short (femtosecond) laser pulses, typically in the wavelength range 750–850 nm, which is achieved by mode-locking of many laser modes with a constant phase relation. This yields a soliton-like propagating pulse within the laser resonator of a very short temporal width. Femtosecond laser pulses facilitate on one hand the examination of very fast transient processes in biology, chemistry and physics and on the other hand proved as a unique tool for lithography and material processing at very high precision. Ultra short laser pulses are mainly demonstrated in Chaps. 2, 3 and 9 with respect to 3D laser lithography and tissure engineering based on non-linear optical processes such as multi-photon absorption.

1.1.2 Laser Processing

The use of lasers in a lithographic apparatus relies on the unique properties of laser radiation, such as high monochromaticity, coherence, directed emission of radiation and excellent beam quality along with high focusability. If the laser substitutes the conventional light source and provides high power radiation at a short wavelength with high spectral density, it illuminates in a simple approach similar to conventional lithography a sample through a patterned mask and projection optics. Alternatively, the laser light can be tightly focused and scanned along a defined path, where it modifies the target upon energy transfer from the beam to the material. Additionally, superimposing multiple laser beams yields, owing to its large coherence length and defined polarization, complex intensity patterns at sub-wavelength resolution, which can be transferred into a suitable photosensitive material. Both methods do not require photolithographic masks for patterning a material and are described in Sect. 1.1.3.1.

The concept of laser processing takes advantage of the high definition of the laser radiation with respect to its high intensity, spatial anisotropy (directionality) and spectral properties [8]. The high intensity of a focused laser sources generally alters the target material in a confined region around the incident laser light. Depending on the optical properties of the material, energy is transferred from the laser into a small volume of the material leading to a local increase of the temperature. The evolution of the temperature is governed by the thermal properties of the target material and the amount of deposited energy. Numerous effects can take place in dependence on the deposited net energy (energy deposition in the volume by the laser minus energy diffusion out of the interaction volume) such as phase changing, melting, evaporation or ablation. At low laser intensities, a gentle heating by the laser is generally induced, while at highest laser intensity explosive material ejection and plasma formation is observed. The main difference between high and very high intensity is the duration in which the energy of the laser is deposited in the material. Short (ns) and ultra-short (ps to fs) pulses deposit the energy on a time scale much smaller than diffusion occurs and the heat cannot spread in the material. This leads to a superheated material and eventually to the mentioned effects (Fig. 1.1).

1.1.3 Biomimetic Processes Involving Laser Radiation

1.1.3.1 Biomimetic Laser-Based Lithography

A straight forward application is to use the laser as *shaping tool* that modifies or creates geometry from or within a target material. The laser acts as a light pencil that draws either in two or three dimensions a structure with a biomimetic shape in a material. The term drawing is quite general and includes processes commonly associated with metals, ceramics or other inorganic materials such as removal (e.g. ablation, etching, milling, drilling, and cutting), joining (welding, sintering), marking or addition (e.g. laser cladding, cusing, laser assisted growth) of material or other

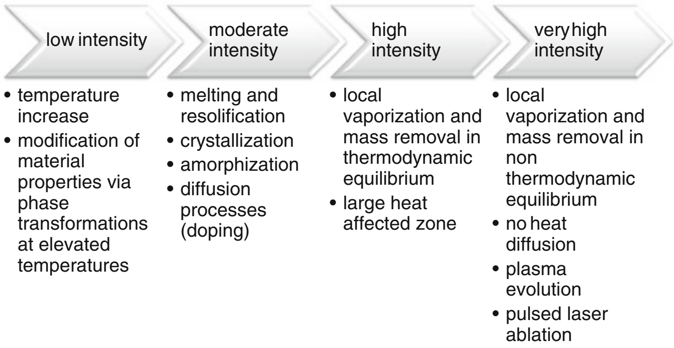

Fig. 1.1 Mechanisms in solid target material at increasing laser intensity

processes like photocrosslinking, photopolymerization, or photoactivation associated with photosensitive organic or biomaterials.

Methods related to laser based shape creation are often termed as rapid prototyping methods and include direct writing methods (direct laser writing–DLW) with a focused laser beam or with multiple interfering laser beams (laser interference lithography–LIL).

Regarding biomimetic applications, the importance of true 3D structuring capabilities of a lithographic method is often emphasized (cf. e.g. Chap. 2). 3D structures can be built by a number of laser based rapid prototyping and fabrication methods (cf. Chaps. 4, 6 and 9) such as (micro-) stereo lithography (μ-SL), selective laser sintering (SLS), or laser additive manufacturing (LAM), which all facilitate a laser-based solid free-form (SFF) fabrication, which are discussed throughout the book chapters. Biomimetic applications of 3D structures are medical implants, such as dental bridges or biologically inspired lightweight structures (cf. Chap. 6).

A common approach for 3D structures is the micro-stereo-lithography (μ-SL) [9], where the shape is built layer-by-layer in a photosensitive material. The pattern in each layer is built either by scanning the focus of a laser or by projecting patterned UV light via masks or a digital mirror device onto the material. The 3D structure is finally built as a layer stack in a repetitive process by vertically translating the material reservoir. This imposes several restrictions on the structure regarding the 3D design (geometrical restrictions due to layer-by-layer processing) and limit the structure resolution. The vertical resolution is limited by the achievable thickness of the individual layers. The lateral resolution is determined from the spot size of the light on the layer. In contrast to the use of conventional UV or VIS lasers in the linear absorption regime of the target material, absorption via inter-band transitions involving more than one photon is a key issue regarding multi-photon based laser lithography, which takes advantage of the strong confinement of the energy transfer of a tightly focused laser beam to a photosensitive material. The energy transfer is responsible for a modification of the material only around the laser focus, which enhances spatial resolution and enables true 3D structuring. The smallest exposed volume element is typically called a voxel and represents the smallest building unit of a 3D structure. μ-SL involving multi-photon based exposure with suitable materials with enhanced spatial resolution was demonstrated for building rather large structures [10].

Multi-photon based laser lithography is a relatively simple method that is inherently capable of 3D structuring, but requires lasers with high peak intensities of the laser pulses. The technological maturity of ultrafast (femtosecond) lasers proved multi-photon-absorption as realistic exposure mechanism with several technical benefits over single-photon exposure. Most important technical benefits of this method are true 3D structuring capabilities and high spatial resolution beyond the diffraction limit (e.g. sub 100 nm structures fabricated with a laser wavelength of 800 nm), which is controlled by the number of applied laser pulses and the laser pulse energy. Finally, this method has found its way to biomimetics as presented in several chapters throughout the book. Recently, Misawa and Juodkazis edited a very comprehensive book about this kind of 3D laser microfabrication [11]. Multi-photon based direct laser writing is a true 3D method that has definitely reached a level of technical perfectness over the last years and may potentially replace other direct writing methods, such as electron-beam lithography in a wide field of applications. It has been applied as a versatile tool in micro- and nano-fabrication anf had been reviewed comprehensively (e.g. [12, 13]) for 3D structures with arbitrary shapes, with freely moving components [14] periodic structures and scaffold structures for photonic and biomedical applications [15, 16], flexible structures for biological cell culture studies [17]. It was also applied to micro replication of biological architectures for cellular scaffolds or custom tissue replacements [18], or in vivo processing of scaffolds with embedded living organisms [19]. Chapter 3 demonstrates biomimetic chiral structures made by 3D laser lithography.

Smooth 2.5D topologies can be achieved with a local variation of the exposure dose with a suitable contrast of the resist. Direct beam writing methods such as direct laser write grey-tone lithography or focused ion beam lithography are capable of fabricating smooth relief structures in photosensitive polymer materials such as commercial positive-tone resists. Due to their inherent capability of varying the exposure dose as a function of the beam position, such methods are often used for the generation of a continuous relief in the target material [20], which could find applications on textured surface with taylored wetting or anti-fouling properties. Often, these structures have a certain periodicity and must cover large surfaces. In such cases, the scanning of a single focused laser beam is a too time consuming process and large areas may not be structured within a reasonable time. For this kind of structures laser interference lithography (LIL) can be used alternatively. LIL is capable of structuring large areas in a single shot exposure (or limited exposure time) without defects and without scanning, but the periodic interference pattern of the laser light limits fabrication to periodic patterns.

The laser provides light of defined wavelength, polarization and coherence, thus enabling coherent superposition of multiple laser beams, whereas the experimental conditions such as laser fluence, film thickness, angle of incidence and polarization of the beams directly correlate to the fabricated patterns.

The beam superposition of multiple laser beams leads to the generation of stable interference patterns, which can be used for patterning films of (usually) positive and negative type photoresist negative type resist, TiO_2 gel films [21], hybrid organic-inorganic sol-gel materials [22], biomimetic tissue [23], as well as PEDOT-PSS [24], a conducting polymer, which is important for organic (opto) electronics. The periodicity of the pattern is determined by difference between the wave vectors of the interfering beams and proportional to the wavelength of the laser and the angle between the interfering beams, which are thus crucial and limiting parameters for the achievable spatial resolution. Depending on the number of beams, angle between the beams and polarization, 1D, 2D, and 3D periodic patterns can be fabricated over a large area in a single exposure step. Multiple exposure steps with rotation and translation of a 1D phase mask facilitate complex 3D patterns such as woodpile structures with three beams [25]. The coherence length limits path differences in the optical setup and determines also the maximal area that can be processed in a single exposure step.

Various types of laser sources such as Nd:YAG lasers at 266 nm (fourth harmonic) or 355 nm (third harmonic) [26] are used for interference lithography. Regarding costs, large area LIL with semiconductor lasers seems more attractive. The used AlInGaN laser has a rather low prize and a long coherence length, which is a pre-requisite for processing large sample areas [27]. Recently, LIL was combined with multi-photon polymerization in a four-beam setup for the fabrication of micro lenses. The four beams were generated using a diffractive optical element and a diaphragm to remove undesired laser light from the optical path. The negative type resist was exposed to multiple laser pulses, which facilitates a much faster processing as compared to multi-photon based direct laser writing, which is a sequential voxel-by-voxel build up process. Appropriate hatching or stepping of the exposed area enables the processing over large areas and reduction of the structure degradation at the edge of the exposed are due to the spatial intensity profile of the laser beams [28]. Originally used for regular 2D patterns, interference lithography is increasingly applied to 3D structures.

1.1.3.2 Biomimetic Laser-Based Coating and Deposition Methods

The previous section introduced the laser as a direct writing tool for the creation of 2D and 3D biomimetic structures. Mimicking the nature by the generation of biocompatible coatings and creating environments for living cells is another aspect of biomimetics that can be dealt with laser technology. In this manner, the laser can be used for the deposition of various biomaterials and research in cell biology. Several methods (laser chemical vapour deposition, laser induced transfer methods, pulsed laser deposition etc.) exist, where the laser is used for the patterned deposition of materials on a substrate. Laser chemical vapour deposition (LCVD) was used for the in situ fabrication of micro lenses with precise control of film properties [5]. This process takes place in a reaction chamber, which contains precursor gases and the substrate. The laser is used to locally heat the substrate, which subsequently dissociates the gas precursor and a thin film deposits on the substrate. Using multiple beams or a layered approach to build the structure, it is possible to create also 3D structures. The deposition rate of LCVD depends linearly on the precursor gas pressure and the laser power density and decreases with increasing scanning speed. The deposition rate can be adjusted by these parameters and is much higher than in conventional CVD [29]. Pulsed laser deposition (PLD) methods, ablation mechanisms and applications are discussed in Chap. 7.

Sensitive materials such as biomaterials that are easily destroyed by the laser are often embedded in a matrix material that absorbs the laser energy. This method (matrix assisted pulsed laser deposition–MAPLE) uses a frozen solvent, which is evaporated upon laser irradiation. The material for deposition is evaporated together with the matrix and deposits on a receiving substrate (cf. Chap. 5). Without masks, the material deposition is unpatterned, hence another method, laser induced forward transfer method (LIFT) is often used for laser assisted patterning (cf. Chap. 8). In the LIFT (sometimes also called laser based bio printing–LBP) process, the laser energy is absorbed in a thin film on a transparent substrate, which leads to droplet formation and ejection of the transfer material. Subsequently, the evaporated material precipitates on a second receiving substrate, which is facing the first substrate either in close (micrometer) vicinity. For soft-matter materials such as polymers or biological compound materials, a direct contact between the substrates was found to yield best transfer results regarding resolution and defined edges of transferred pixels [30].

LIFT can be achieved with various types of lasers (UV excimer lasers, Nd:YAG, Ar-ion lasers, fs lasers). The transfer materials are often sensitive to oxygen or humidity, thus requiring a vacuum or inert gas setup. Originally used for the patterned transfer of metal films, it can be applied for a variety of materials including oxides and biomaterials or even more complex multi-layer systems such as a polymer light emitting diode pixel [31] or organic thin film transistors [32]. Such sensitive materials or materials, which are transparent to the incident laser or easily destroyed by the incident laser, can be transferred by using an energy absorbing sacrificial layer (dynamic release layer) between the transfer material and the carrier, which promotes the release of the material. Additionally, the temporal shape of ultrafast laser pulses influences the LIFT process and the achievable resolution on the receiving substrate, which is attributed to fast electron and lattice interactions. It was shown that fs pulses with a short separation (less than 500 fs) show large impact of the deposited pixel size, while the covered area stays constant for longer pulse separations up to 10 ps [33].

Using microsphere arrays as micro lenses, parallel material transfer (parallel LIFT) with an unfocused laser beam can be achieved [34]. Polystyrene beads are on top of a transparent substrate (quartz glass) and focus the incident light onto the single or multi-layered transfer material, which is on the other side of the substrate. Thus, micron to sub-micron holes can be written into the films and corresponding dot patterns on the receiving substrate.

1.1.3.3 Biomimetic Laser-Based Biomaterial Processing and Tissue Engineering

From a materials point of view, the laser supports rapid tooling for natural biopolymers (e.g. proteins, polysaccharides) and artificial biomolecules (PLA, PGA, PLGA etc.). Laser radiation offers the possibility to generate 3D biological microstructures (scaffolds) by crosslinking of oxidizable side chains in biomolecules. The purpose is the creation of chemically and physically defined cell environments for applications such as tissue regeneration and gene delivery as described in Chaps. 2, 9, and 10.

In the field of tissue engineering, which is closely related to replace or repair tissue such as bone, cartilage, blood vessels, bladder, skin, muscle etc. the control of cell density and organization is crucial. Laser based method such as laser assisted bioprinting implementing the laser induced forward transfer can deposit patterned films of bioink on substrates. Chapter 8 discusses examples of printed cell types.

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