Chapter 1
Introduction

Abstract In this chapter we give a short history of the laser tools in comparison to the classical tools and present the main characteristics and applications of pulsed laser ablation process. We show that due to the unique properties of the laser beams (such as coherence, monochromaticity and collimation) they are applied in several research and practical fields. In some applications, such as atomic fusion and isotope separation, the laser power is very important. In other applications, the main reason for using laser lies in its monochromaticity and coherence (pollution detection, length/velocity measurement, interferometry, etc.), low divergence (laser show, pointer/guide, audio-player), or a combination of all of them (communication, holography, metrology). Accordingly, over the last several decades there were developed many types of lasers capable of delivering a wide variety of wavelength, energy, temporal/spectral distribution and efficiency. Typical commercially available lasers for material processing are: solid state crystal or glass lasers (e.g. Nd-YAG, Ruby lasers), semiconductor lasers (AlGaAs, GaAsSb lasers), dye or liquid lasers solutions of dyes in water/alcohol and other solvents, neutral or atomic gas lasers (HeNe laser, Cu or Au vapour laser), ionized gas lasers or ion lasers (argon (Ar) and krypton (Kr) ion lasers), molecular gas lasers (CO₂ or CO lasers), and excimer lasers (XeCl, KrF). Pulsed laser ablation (PLA) represents the material removal process caused by nanosecond and pico-/ femtosecond lasers. PLA is employed for micro- and nano-patterning of materials, the cleaning of surfaces from contamination layers and particulates, for chemical analysis of materials including liquids, and for various applications in biotechnology and medicine. The advantage of PLA in micro processing over the classical mechanical and thermal methods comes from the strong spatial and temporal localization of the laser-mater interaction which gives very large heating/cooling rates (as large as 1,000 K/ns).
1.1 Short History: Classical Tools Versus Lasers Tools

Laser is surely one of the greatest innovations of 20th century. Its continuous development has been an exciting chapter in the history of science, engineering and technology. As a versatile source of pure energy in a highly concentrated form, laser has emerged as an attractive tool and research instrument with potential for applications in an extraordinary variety of research and industrial fields.

The initial foundation of laser theory was laid by Einstein [1]. Subsequently, Kopfermann and Ladenburg [2] presented the first experimental confirmation of Einstein’s prediction. In 1960, Maiman [3] developed a ruby laser for the first time. This was followed by much basic development of lasers from 1962 to 1968. Almost all important types of lasers including semiconductor lasers, Nd-YAG lasers, CO₂ gas lasers, dye lasers and other gas lasers were invented in this era. After 1968, the existing lasers were designed and fabricated with better reliability and durability. By mid 1970s more reliable lasers were made available for truly practical applications in the industrial applications such as cutting, welding, drilling and marking. During the 1980s and early 1990s the lasers were explored for surface related applications such as heat treatment, cladding, alloying, glazing, and thin film deposition.

Due to the unique properties of the laser beams (e.g. coherence, monochromaticity and collimation) they are applied in several research and practical fields. Depending on the power, the applications domains of the lasers are as follows [4, 5]:

(a) low power/intensity lasers can be employed in:

- communications: optical fiber communications, telecommunications, optical data storage;
- metrology: holography, distances and velocity measurements, interferometry, alignment;
- reprography: printings, scanning, data storage;
- entertainment: laser beam show, pointers, audio-video recording;

(b) high power/intensity lasers can be employed in:

- military: weapon, weapon guide;
- chemical: spectroscopy, photo-chemical deposition, pollution control;
- medical: surgery, dentistry, tumor therapy, dermatology;
- heat source: forming, hardening, welding, coating, laser deposition, laser ablation;
- scientific: laser fusion, coherent ultra-short X-ray beams for analysis of atomic structure, particle acceleration.

In some applications, such as atomic fusion and isotope separation, the laser power is very important. In other applications, the main reason for using laser lies in its monochromaticity and coherence (pollution detection, length/velocity measurement, interferometry, etc.), low divergence (laser show, pointer/guide, audio-player), or a combination of all of them (communication, holography, metrology). Accordingly,
over the last several decades there were developed many types of lasers capable of delivering a wide variety of wavelength (wavelengths of presently available lasers cover the entire spectral range from the far-infrared to the soft X-ray.), energy, temporal/spectral distribution and efficiency [6]. An overview on the laser intensities available in the last 50 years (and the envisaged laser facilities by the end of 2020) with their potential practical and scientific applications is given in Fig. 1.1. Different laser facilities worldwide with their in-focus intensities are also indicated.

Lasers employed for materials processing range from those with a high peak power and extremely short pulse duration to lasers with high-energy and continuous-wave output. Table 1.1 summarizes the commercially available lasers and their main areas of application bauerle [5]. Depending on the required type of laser emission (duration, power and wavelength), the laser active medium could be solid, liquid or gaseous. The lasers are commonly named according to the state or the physical properties of the active medium. Consequently, there are solid state lasers (with crystals, glasses or semiconductors), liquid lasers, and gas lasers. The gas lasers can be further subdivided into neutral atom lasers, ion lasers, molecular lasers and excimer lasers. Typical commercially available lasers for material processing are:

- solid state crystal or glass lasers: Nd-YAG, Ruby lasers;
- semiconductor lasers: AlGaAs, GaAsSb and GaAlSb lasers;
- dye or liquid lasers solutions of dyes in water/alcohol and other solvents;
Table 1.1 Commercially available lasers and their applications

<table>
<thead>
<tr>
<th>Laser</th>
<th>Year of discovery</th>
<th>Commercialised since</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruby</td>
<td>1960</td>
<td>1963</td>
<td>Metrology, medical applications, inorganic material processing</td>
</tr>
<tr>
<td>Nd-Glass</td>
<td>1961</td>
<td>1968</td>
<td>Length and velocity measurement</td>
</tr>
<tr>
<td>Diode</td>
<td>1962</td>
<td>1965</td>
<td>Semiconductor processing, biomedical applications, welding</td>
</tr>
<tr>
<td>He-Ne</td>
<td>1962</td>
<td>1966</td>
<td>Light-pointers, length/velocity measurement, alignment devices</td>
</tr>
<tr>
<td>CO₂</td>
<td>1964</td>
<td>1966</td>
<td>Material processing-cutting/joining, atomic fusion</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>1964</td>
<td>1966</td>
<td>Material processing, joining, analytical technique</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>1964</td>
<td>1966</td>
<td>Powerful light, medical applications, material processing</td>
</tr>
<tr>
<td>Dye</td>
<td>1966</td>
<td>1969</td>
<td>Pollution detection, isotope separation, scientific purposes due to wavelength tunability</td>
</tr>
<tr>
<td>Cu</td>
<td>1966</td>
<td>1989</td>
<td>Isotope separation</td>
</tr>
<tr>
<td>Excimer</td>
<td>1975</td>
<td>1976</td>
<td>Medical application, material processing, colouring</td>
</tr>
<tr>
<td>Ti-Sapphire</td>
<td>1982</td>
<td></td>
<td>Scientic purposes: tunable ultrashort laser pulses due to the large bandwidth</td>
</tr>
</tbody>
</table>

- neutral or atomic gas lasers: HeNe laser, Cu or Au vapour laser;
- ionized gas lasers or ion lasers: argon (Ar) and krypton (Kr) ion lasers;
- molecular gas lasers: CO₂ or CO lasers;
- excimer lasers: XeCl, KrF, etc.

Soon after the invention of the laser, it was recognized that the focused beam can be used as a tool for material removal. Pulsed laser ablation (PLA), representing the material removal process caused by nanosecond and pico-/femtosecond lasers, has been discussed in [4, 7, 8]. The PLA technique is employed for micro- and nano-patterning of materials, the cleaning of surfaces from contamination layers and particulates (devices, artwork, buildings), for chemical analysis of materials including liquids (LIBS, MALDI, etc. [9–11]), and for various applications in biotechnology and medicine (laser micro-dissection, cleaning, sterilization, fabrication of implants, correction of the cornea, dermatology, surgery, etc.). While many of these processes can be performed, in principle, in vacuum or an inert atmosphere, some types of surface modifications and the synthesis of special types of nanoparticles and powders require a reactive medium.

The advantage of PLA in micro processing over the classical mechanical and thermal methods comes from the strong spatial and temporal localization of the laser-mater interaction which gives very large heating/cooling rates (as large as 1,000 K/ns [4, 12, 13]) and small volumes that are subjected to the thermal induced...
defects beyond the removed material. Thus, PLA is the adequate method for processing brittle and thermal sensitive materials. Due to the non-contact nature of PLA, it enables patterning of non-planar work-pieces, in contrast to other conventional surface patterning techniques.

In industrial processing, lasers generating pulses with energies of the order of J can drill metallic plates thicker than one millimeter in less than one millisecond. However, a lack of geometrical accuracy and other quality problems resulting from recast material strongly limited the number of industrial applications [14].

Unique is the property that pulsed lasers allow to heat material at strongly localized areas, leaving the surrounding material practically unaffected. For materials with high thermal conductivity (metals and certain semiconductors) the high quality surface patterning by PLA can only be achieved with picosecond or femtosecond laser pulses. This is because the heat affected zone (HAZ) becomes very small when using short pulses since the HAZ dimensions are determined mainly by the thermal diffusion length \( l_{th} \) which scales with pulse duration [4]:

\[
l_{th} = 2\sqrt{D\tau_p}.
\]  

(1.1)

More generally, the penetration to which a laser pulse interacts with the material is determined by the optical and thermal penetration depths:

\[
l = l_\alpha + l_{th}.
\]  

(1.2)

In dielectrics, optical penetration depth dominates over the thermal one and is a strong function of the laser wavelength. In metals, on the other hand, the optical penetration depth turns out to be smaller than a tenth of the wavelength and can be neglected in most cases.

It has to be made clear at this point that \( l_\alpha \) and \( l_{th} \) gives only qualitative estimation of the accuracy of laser processing. The quantitative values for the depth to which material is molten or vaporized depend additionally on the energy density (i.e. laser fluence) transmitted to the target.

The same is true for the lateral dimension of the structure. Only seldom the diameter \( d_f \) of the laser beam on the target surface coincides with the diameter of the processed (ablated) zone \( d_{abl} \). For a Gaussian beam, \( d_{abl} \) at a given laser fluence \( F \) is demonstrated to depend on \( d_f \) and the threshold laser fluence for ablation \( F_0 \) [14]:

\[
d_{abl} = d_f \sqrt{\frac{1}{2} \ln\left(\frac{F}{F_0}\right)}.
\]  

(1.3)

The edges of the beam with energy density below the threshold for material removal may act on the work piece in an unwanted way by causing thermal damage. A steep limitation of the beam is desirable for a treatment with high quality, therefore. On the other hand, the sharpness of the laser beam may be affected by laser induced plasmas near the ablation front (or by gas breakdown in front of the work piece).
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(a) (b)

Fig. 1.2 a Process strategies to achieve high accuracy in laser drilling [14]. b Material removal calculated for aluminum with piston model [14–16]

The ablation volume is determined by penetration depth and spot diameter. The reduction of the laser pulse duration, beam diameter on target and laser pulse energy is expected to lead to a decrease of the interaction volume, which can be used to increase the accuracy of a removal process (see Fig. 1.2a).

The phase composition of the removed material strongly depends on the laser fluence. Figure 1.2b shows the results of a calculation [15] based on von Allmen’s piston model [16]. The plot makes clear that increase of the laser intensity leads to increase of the share of vaporized material at the expense of molten material. From this point of view, the high laser fluences appear favorable for achieving high accuracy, to some extend a contradiction to the previous findings.

1.2 Solid Materials (Metals, Semiconductors, Dielectrics) to be Processed by PLA

Among the inorganic materials where patterning by PLA is advantageous are oxidic perovskites and different types of oxides including glasses [8, 17–22]. Recent applications include the fabrication of micro-optical devices such as micro-mirrors [23], fiber optical devices [24, 25], graded transmission dielectric and metal thin films masks [26, 27], the micromachining of thin films for applications in solar cell production [28, 29], and the fabrication of masters that are subsequently used as molding tools [30], etc.

First experiments on PLA of organic polymers have been reported in [31, 35], Kawamura 1982. While the results of these investigations were originally described on the basis of purely photochemical processes (direct bond breaking) it has been shown later that for most types of polymers and for wavelengths $\lambda > 200$ nm, photophysical or even purely thermal processes are dominating [32–34]. In case of PI, 302 nm Ar+ laser irradiation at sub-threshold ablation fluences resulted in hump
formation due to scission of polymer chains and the depletion of small fragments [33]. This explains the differences in ablation rates derived from stylus [35] and quartz crystal microbalance (QCM) measurements [32]. In the latter, an Arrhenius tail in the ablation rate was observed. These measurements should, however, be repeated by using after each single laser shot a new material surface.

Nanosecond PLA may be employed in:

- cluster and nanoparticle formation;
- laser cleaning, including art conservation and restoration [36–38];
- chemical analysis [4, 39, 40];
- in biological and medical applications [41–48].

The modeling of nanosecond PLA has been described in [4, 7]. In most materials, the excitation energy is rapidly dissipated into heat. The laser-induced temperature rise either directly or indirectly causes ablation and plasma formation. In the latter case, volume changes and the formation of stresses and defects play an important or even a dominating role. Direct, non-thermal bond breaking may become important for polymer ablation at wavelengths smaller than 200 nm. This has been verified in a number of investigations, dealing with 157 nm F2 laser ablation of PMMA and PTFE [49–51].

Picosecond and femtosecond lasers permit patterning of materials that cannot be patterned by means of nanosecond pulses, or not in a well-defined way. Among those are thermally high conductance materials, wide-bandgap materials, and transparent glasses and polymers.

With ultrashort pulses, multiphoton optical absorption/ionization within both the substrate material and the ambient medium, non-equilibrium effects related to electronic and/or vibrational excitations, avalanche breakdown, and Coulomb explosion become important or even dominating. Such strongly non-linear interaction processes can further enhance or diminish the localization of the excitation energy. This, in turn, can increases or diminishes the resolution in surface patterning, and also opens up completely novel material processing possibilities.

### 1.2.1 Thermally Well-Conducting Materials

For materials with large thermal diffusivity, damage-free patterning and drilling requires picosecond or even femtosecond pulses. This has been demonstrated for metals [52–54], many types of semiconductors, and for thin films of high-temperature superconductors [55]. As long as the laser-pulse duration exceeds the electron-phonon relaxation time, the width of the heat-affected zone (HAZ) can be estimated from the heat penetration depth given by Eq. (1.2). Thus, with ultrashort pulses, the HAZ can be significantly reduced, or even avoided completely. Clearly, the width of the HAZ depends not only on material parameters and on pulse duration but also on laser fluence, pulse-repetition rate and, with thin films, on film thickness and the type of substrate material.
Many of the mechanisms and models discussed in connection with nanosecond-laser ablation, hold also with pulses that are longer than several 10 to 100 picoseconds [4].

With shorter pulses, however, new phenomena are observed. Among those is the energy transport by ballistic and hot electrons, which become important, in particular with noble metals and fs-laser pulses [56, 57]. The experimental data can be well described by the two-temperature model [4, 58, 59].

### 1.2.2 Wide-Bandgap Materials, Glasses, Polymers

Ultrashort pulses can be used in patterning and micromachining of materials for which the photon energy of practical lasers is not high enough either for efficient single-photon absorption or defect generation. Among these materials are wide-bandgap materials with $E_g > h\nu$, but also glasses and polymers with low absorptivity. Ultrashort laser pulses permit precise patterning of these materials due to their very high intensity which induce non-linear processes within the irradiated materials. Examples for wide-bandgap materials are alkali and earth-alkali halides, and various oxides, such as $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, etc. Among the amorphous materials investigated in great detail are $\text{a-SiO}_2$ and glass filters. Real and potential applications include the drilling of deep holes, 3D patterning within materials [60–62], micromachining of materials for micro-optical and optoelectronic devices such as gratings [63] and waveguides [64, 65], material modifications for optical data storage [66], etc.

### 1.3 Practical Applications of PLA and General Aims

Laser processing allows material transformations (e.g. doping, hardening), material removal (e.g. ablation, etching), and material deposition (e.g. CVD, PLD) by means of laser radiation. Processing with lasers takes advantage of the characteristics of laser light, e.g. high spatial coherence, high temporal coherence, monochromaticity, directionality. Commercially available lasers have pulse durations from continuous wave down to femto-seconds, providing output powers up to PW.

#### 1.3.1 PLD

The laser beam interacting with matter could lead to extraction of atoms, clusters and even droplets from the target material by the so called ‘ablation process’. These generated particles heave an initial speed that could reach values of tens of kilometers per second but is gradually decreasing while interacting with ambient atmosphere.
1.3 Practical Applications of PLA and General Aims

For some applications is important to collect the ablated particles on a particular surface, the most usual case being the deposition of a thin film for coating a plane surface. Pulsed laser deposition (PLD) is thus obtained by placing an object surface in front of the ablation plume, part of the particles hitting the surface while some of them will remain on it, gradually forming a thin film. The reason of PLD coating of a surface is usually the fact that the coating will give to the object surface significantly different properties as compared to the original material. The target surface could become harder, non-corrosive, conductive and so on while the rest of the object properties will remain the same.

1.3.2 Cluster Formation by PLA

The synthesis of nanomaterials by laser vaporization and pulsed-laser ablation of solid targets in inert or reactive gases or liquids is a rapidly growing field of research. The method involves the condensation of atoms/molecules and cluster formation (with or without any chemical reactions) during the fast expansion of the vapor/plasma plume generated in front of a target. The time of nucleation and the size and composition of clusters depend on the type of material, the laser parameters, and the ambient medium. The technique supports fabrication of various nanomaterials with controlled size distribution and different physical/chemical properties. Among these are particles with amorphous, poly- or single-crystalline microstructure, coated particles, shell spheres, nanowires, nanotubes, nanohorns, etc [8].

1.3.2.1 Clusters in Vacuum and Gaseous Ambient

Cluster formation during plume expansion has been studied mainly for background atmospheres of noble gases, and of N₂ and O₂ at pressures up to several hundred mbar. Experimentally, the dynamics of cluster formation was studied in situ by time-resolved optical spectroscopy, including emission and absorption spectroscopy, laser-induced photoluminescence, Rayleigh scattering (RS), X-ray absorption spectroscopy, etc. Among the target materials employed are metals such as Ni [67], CoPt alloys [68, 69], and semiconductors, in particular Si/SiOₓ [70–72] and ZnTe [73].

Carbon targets have been employed to study the formation of carbon clusters [74, 75], nanohorns [74, 76] and, in the case of Co- or Ni-doped targets, the growth of nanotubes [74, 77, 78]. Mainly ceramic targets were used for the synthesis of oxide clusters [79] including high-temperature superconductors such as YBa₂Cu₃O₇ (YBCO) [80], CaₓFeₙO₂ [81], and glasses [82]. Particulates accompanying laser ablation of PTFE targets have been studied by Heitz and Dickinson [83].

The synthesis of compounds formed in reactive atmosphere has been studied for a number of materials, e.g., for Ni. Depending on the laser parameters and the O₂ pressure, PLA results in the formation of NiO cubes or Ni/NiO core/shell spheres
Detailed studies on the dynamics of cluster formation during plasma plume expansion have been performed for silicon and carbon [74].

1.3.2.2 Clusters in Liquid Ambient

Laser ablation and cluster formation within liquid media has been studied for metals such as Au [84], Ag [85], Gd [86], Ti [87, 88], and for different alloys. Among the semiconductors studied in detail were Si [88, 89] and II–VI compounds [90]. Ablation and cluster formation has been studied also for oxides and polymers [91]. In most of these experiments, particle-size distributions have been investigated as a function of laser fluence for multiple-pulse irradiation. Thus, fragmentation of clusters and/or ablation products within the suspension during subsequent pulses will be very important. Furthermore, with the pulse-repetition rates employed, the local laser-induced temperature rise results in convective flows (micro-stirring) within the liquid. Convection will influence the local concentration of product species and thereby the efficiency of subsequent fragmentation processes. For these reasons, an analysis of particle-size distributions on the basis of fundamental interaction processes is very difficult. Nevertheless, PLA and laser fracture in liquids are versatile techniques for the fabrication of colloidal solutions and nanoparticle powders of various types.

1.3.2.3 Micro- and Nano-Structuring of Materials

There is continuous effort in developing new techniques for micro- and nano-structuring of materials in order to create small features structures on large areas at high speed. This effort is driven by the demands of modern science and technology. For example, the development of two-dimensional (2D) patterns and thin film growth techniques is useful in microelectronics industry. The performance of the micro and nano-processing techniques can be characterized by the Tennant’s empirical law [92, 93].

\[
\text{feature size (nm) } = 23 \times \left[ \text{throughput} \left( \mu \text{m}^2/\text{h} \right) \right]^{1/5},
\]

which establishes the relationship between the structure resolution and throughput of the technique. The law indicates that the fabrication of large structures becomes very slow as the size of typical resolution decreases.

The three-dimensional (3D) structures can add new functionality to the planar 2D devices facilitating miniaturization and making them faster. In recent decades, techniques for 3D structuring of materials have become important tools for the fabrication of photonic crystals [94, 95] and other micro-and nano-structures with novel photonic functions [96–98].
References

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