Abstract

Laser ablation is the process in which material is removed from the sample surface by irradiating it with laser beam. Laser ablation by the nanosecond or longer laser pulses has traditionally been viewed as resulting from rapid heating of the surface layer. The temperature rise can result in material vaporization with or without melting. This is known as thermal laser ablation. With recent development of the ultra-short pulsed lasers it has become increasingly clear that electronic effects play a significant, and possibly dominant, role in laser ablation process. Particle ejection governed by electronic mechanisms is called non-thermal laser ablation.
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1 Introduction

Laser ablation is the process of removing material from a solid surface by irradiating it with a laser beam. Material removal caused by short high-intensity laser pulse is often termed pulsed-laser ablation (PLA).

Upon impact of a laser beam on a material, electromagnetic energy can interact with elementary excitations that are optically active. Among those are different types of electronic excitations (interband and intraband excitations, excitons, plasmons, etc.) and excitations of phonons, polaritons, magnons, etc [1, 2]. In addition, there may be localized or non-localized electronic or vibrational states that are related to defects or impurities. In the whole process the molecular structure as well as the shape of the material is changed in various ways. The ejected material may include neutral atoms and molecules, positive and negative ions, clusters, electrons and photons. The generated plasma may have electron temperatures of thousands of degrees. Understanding this sequence of events requires knowledge from several branches of physics.

Laser ablation strongly depends on the laser characteristics and on the target properties. The laser pulse duration and irradiance are the most important factors for defining ablation conditions. The main effect in ablation of any solid surface is absorption of the laser radiation which depends on the laser light energy. The primary energy related parameters influencing the laser material interaction are fluence (energy per unit area [J/cm²]) and irradiance or intensity (energy per unit area and time [W/cm²]). Significant material ablation is observed only if the laser fluence exceeds certain threshold fluence. The threshold fluence depends on the particular material and on the laser parameters. Typically values are between 0.1 J/cm² and several J/cm².

Another important parameter in laser ablation process is the laser wavelength. Shorter wavelengths offer higher photon energies for bond breaking and ionization processes. Secondly, the wavelength can be limiting factor in the size of beam on the surface. The shorter the wavelength the easier it is to focus to small beam diameters. Another effect is in the amount of absorption that occurs in any plasma that is produced on the surface or in the cavity. Plasma absorption is much more problematic when going to the longer wavelengths [3].

In addition to the mentioned parameters, some other parameters are also very important; laser beam profile, repetition rate, etc. The influence of environmental ambient (gas and pressure) and sample’s properties on laser ablation must also be considered.

Regardless of detailed mechanisms, many important applications depend on laser ablation. These include industrial processes such as laser hole drilling or other micromachining, materials processing to produce thin films or microstructures, chemical analysis, biomedical uses, propulsion, etc [1, 2, 4, 5].

2 Interaction of laser light with matter

When laser beam strikes a surface it undergoes a reflection, absorption and transmission. For the perpendicularly incident beam the reflection is given by the Fresnel expression [6]:

\[
R(\lambda, T) = \frac{(1 - n(\lambda, T))^2}{(1 + n(\lambda, T))^2}
\]  

(1)

where \(n(\lambda, T)\) is the refractive index of the material.
For absorbing or conducting dielectric materials $n$ is complex number:

$$n = n' + in'' = \varepsilon^{1/2} = (\varepsilon' + i\varepsilon'')^{1/2}$$

(2)

where $\varepsilon$ is the complex dielectric function. Dielectric function can be regarded as generalized response function of the material. The real and imaginary parts of $n$ and $\varepsilon$ are related by

$$n'^2 = \frac{|\varepsilon| + \varepsilon'}{2} \quad \text{And} \quad n''^2 = \frac{|\varepsilon| - \varepsilon'}{2}$$

(3)

The dielectric function fully describes the response of a material to weak electromagnetic irradiation. As the laser beam passes through a new medium it is absorbed according to Beer Lambert’s law,

$$I = I_0 e^{-\mu x}$$

(4)

where $I_0$ is the intensity entering the surface and $\mu$ is the absorption coefficient $[m^{-1}]$. Absorption coefficient is defined as

$$\mu = \frac{4\pi}{\lambda} n''$$

(5)

The absorption coefficient depends on the medium, wavelength (Figure 1) and the intensity of the radiation and the temperature of the material. The inverse of $\mu$ is referred as absorption length or penetration depth.

![Figure 1: Absorption coefficient of silicon. The absorption maximum is at 300 nm [7].](image)

**Nonmetals**

Semiconductors and insulators have in their ground state only bound electrons. In the classical model the electron is represented as harmonic oscillator driven by the force of the electric field. For nonmetals the dielectric function is

$$\varepsilon = 1 + \frac{Ne_0^2}{\varepsilon_0 m_e \omega_0^2 - \omega^2 + i\Gamma \omega}$$

(6)

where $N$ is the number of bound electrons, $\omega_0$ is resonance frequency, $\omega$ is light frequency and $\Gamma$ is damping constant.
Metals
The optical response of a metal is dominated by the conduction electrons. Since the electron gas is degenerate, only electrons in states close to Fermi level, referred to as free electrons, can contribute to the optical properties. The dielectric function of a free-electron metal can be obtained from (6) by setting the resonance frequency equal to zero and by replacing the damping constant \( \Gamma \) by the inverse collision time \( \tau_e \). The resulting expression is

\[
\varepsilon = 1 - \omega_p^2 \left[ \frac{\tau_e^2}{1 + \omega^2 \tau_e^*} + i \frac{\tau_e^2}{\omega \tau \left(1 + \omega^2 \tau_e^*\right)} \right]
\]

where

\[
\omega_p = \sqrt{\frac{N e^2}{\varepsilon m_e}}
\]

is the electron plasma frequency. At \( \omega = \omega_p \) both \( \varepsilon' \) and \( n' \) vanish.

3 Laser ablation

Laser ablation is a process which starts with absorption of the laser radiation followed by electronic excitation which may give rise to thermal or electronic mechanism of particle ejection. The two mechanisms are called thermal and non-thermal (photochemical) laser ablation [1, 2, 5]. The borderline of these two mechanisms although exists is very difficult to define. When both thermal and non-thermal mechanisms contribute to ablation process, then the process is called photophysical ablation. Figure 2 shows block diagram for different channels in PLA. In thermal ablation the excitation energy is instantaneously transformed into heat. The increase in the temperature changes the optical properties of the material and thereby the absorbed laser power. The temperature rise can result in thermal material ablation (vaporization) with or without melting. Non-thermal laser ablation takes place if the photon energy is high enough. In this case laser-light excitations can result in direct bond breaking. As a consequence, single atoms, molecules, clusters or fragments desorb from the surface. The process can take place without any change in surface temperature. Besides the direct channels of laser ablation described above, there is an indirect channel. The temperature rise or laser induced defect can build up stress which results in mechanical ablation.

![Figure 2: Different mechanisms involved in PLA. Solid arrows are for direct channels and dashed arrows for indirect channels of PLA (derived from [2]).](image-url)
3.1 Interaction of high-intensity laser light with matter

On excitation with a high-energy laser pulse, a material undergoes several stages of relaxation before returning to equilibrium. The energy is transferred first to electrons and then the lattice. The interaction includes several regimes of carrier excitation and relaxation. We can distinguish the following four regimes: (1) carrier excitation, (2) thermalization, (3) carrier removal and (4) thermal and structural effects [1, 2, 6, 8]. These regimes and the timescales for the corresponding processes are shown in Figure 3. The various processes shown do not occur sequentially; they overlap in time, forming a continuous chain of events spanning the entire range from femtoseconds to microseconds.

![Figure 3: Timescales of various electron and lattice processes in laser-excited solids. Each green bar represents an approximate range of characteristic times [8].](image)

**Carrier excitation**
In insulators and semiconductors high energy laser pulse can generate electron-hole pairs via various excitation processes (explained in section 3.4). Next, the free carrier absorption increases the energy of carriers in the electron–hole plasma or that of initially free electrons in a metal. If some of the carriers are excited well above the bandgap (or Fermi level in a metal), impact ionization can generate additional excited carriers. Excitation of the valence electrons results in destabilization of the covalent bonds. Atoms may thus gain sufficient kinetic energy to break weakened bonds which may lead to particle ejection which is known as non-thermal ablation.

**Thermalization**
After the laser energy is delivered to the system, the carriers quickly relax through several processes (carrier-carrier and carrier-phonon scattering). The emitted phonons carry little energy and therefore it takes many scattering processes (several picoseconds), before carriers and the lattice reach thermal equilibrium.

**Carrier removal**
Although the carrier distribution has the same temperature as the lattice due to thermalization, there is an excess of free carriers compared to that in the true thermal equilibrium. These carriers can be removed in two ways: recombination of electrons and holes (radiative or non-radiative recombination), or diffusion of carriers away from the excitation region.
Thermal and structural effects
When the free carriers and the lattice come to an equilibrium temperature the material is essentially the same as the heated by the conventional means. If the lattice temperature exceeds the melting or boiling point, melting or vaporization can occur. This is known as thermal ablation. If no phase transition occurs, the temperature reverts back to the ambient value on the timescale of microseconds.

3.2 Thermodynamics

The classical picture of thermal vaporization from heated surface is true for moderate laser fluences at time scales that allow establishment of local thermal equilibrium. That would be the case for nanosecond laser irradiation because relaxation times in most materials are in subpicosecond regime. The energy coupling into target material is determined by the material optical properties, that is, complex refractive index \( \mu \). The energy absorbed by the material at a depth \( z \) from the surface [1, 2], for temperature dependent absorption coefficient, is given by

\[
Q_{\text{abs}} = (1 - R) I_o \mu(T(z)) \exp \left( \int_0^z \mu(T(z')) \, dz' \right)
\]  

(9)

where \( R \) is the surface reflectivity (1) and \( \mu \) absorption coefficient. For nanosecond laser pulses, the electron and the lattice are at thermal equilibrium, characterized by a common temperature \( T \). The transient temperature field can then be calculated by solving the heat conduction equation:

\[
\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k(T) \nabla T) + Q_{\text{abs}}
\]  

(10)

where \( \rho, c_p, k \) and \( T \) represent density, specific heat for constant pressure, thermal conductivity \([W/mK]\) and temperature, respectively. These properties in general are functions of temperature. The solution of the heat equation requires knowledge of the initial and boundary conditions. We can define thermal heat diffusivity \( \alpha \left[ m^2 / s \right] \) as the ratio of thermal conductivity to volumetric heat capacity:

\[
\alpha = \frac{k}{\rho c_p}
\]  

(11)

Depth \( l \), to which heat penetrates in time \( t \), is given by \( l = \sqrt{4 \alpha t} \). With this equation we can determine the pulse duration that the heat penetrates to the desired depth.

If the laser energy exceeds the threshold energy for melting and evaporation, we can calculate the temperature distribution from the heat equation (10) when the latent heats of melting and evaporation are taken into account. The convenient way to incorporate latent heats into heat equation is to describe phase changes with the enthalpy method. The simple heating picture presented does not address nonlinear issues or optical generation of free carriers in semiconductors and insulators. Therefore, this simple heating model is more suitable for metallic materials.

3.3.1 Two temperature model

For ultrashort (picosecond or femtosecond) laser pulses, the electron and the lattice are not at thermal equilibrium. In this model the electron and lattice system are treated as two separate heat baths with temperatures \( T_e \) and \( T_l \).
The two main equations of the one dimensional two temperature model [1, 9, 10] are as follows:

\[
C_{e}(T_{e}) \frac{\partial T_{e}}{\partial t} = - \frac{\delta}{\delta z} \left[ k_{e} \frac{\partial T_{e}}{\partial z} \right] - g (T_{e} - T_{l}) + S(z,t) \tag{12}
\]

and

\[
C_{l}(T_{l}) \frac{\partial T_{l}}{\partial t} = g (T_{e} - T_{l}) \tag{13}
\]

\(C_{e}\) and \(C_{l}\) are the electronic and lattice heat capacities, \(k_{e}\) is the electronic thermal conductivity, \(S(z,t)\) is the absorbed laser energy density per unit time (source term) and \(g\) is electron – phonon coupling constant. The greater \(g\), the greater the rate of heat transfer between the electrons and the lattice and hence the faster the thermalization between electronic and lattice subsystem. Equation (12) describes electronic heat diffusion with the first term. The second term describes electron – phonon coupling and the third term describes the heating of the electrons by the laser pulse. The heat diffusion through the lattice is neglected in the second equation (13). The two temperature model is a system of coupled differential equations, which in general can not be solved analytically.

3.3 Plasma consideration

Vaporized mass can be ionized by absorbing the incoming laser beam, forming a plasma. Laser radiation is absorbed primarily by inverse Bremsstrahlung. The inverse Bremsstrahlung involves the absorption of a photon by free electrons during the collision with heavy particles (ions and atoms). A third particle (ion or atom) is necessary for energy and momentum to be conserved during absorption. Inverse Bremsstrahlung absorption is dominant mechanism when operating with longer wavelengths (IR). Photoionization, multi-photon ionization and impact ionization in the vapor also contributes to this process, if the laser intensity is high enough and laser wavelength is short [2, 3, 11]. When the plasma plume is near the critical density, the later part of the laser beam pulse energy would be partially absorbed before it reaches the target. That is known as plasma shielding. Plasma shielding is important phenomenon in nanosecond laser ablation but can be neglected in femtosecond time regime. During picosecond or femtosecond pulse almost no plasma plume can develop and plasma shielding is reduced or even avoided.

3.4 Ablation mechanisms

When laser beam acts on a material, laser energy is first absorbed by electrons. The absorbed energy propagates through the electron subsystem, and then is transferred to the lattice. In this way laser energy is transferred to the ambient target material. One can distinguish three characteristic time scales [11]:

- \(t_{e}\) the electron cooling time, which is in the order of 1ps;
- \(t_{l}\) the lattice heating time; and
- \(t_{p}\) the duration of laser pulse.

Both \(t_{e}\) and \(t_{l}\) are proportional to their heat capacity and are material dependent. Heat capacity of electron is much less than that of lattice, so \(t_{e} \ll t_{l}\). The temporal distributions of energy fields at different time scales, can greatly affect the interaction between energy and material.
For different ranges of $t_p$ we can distinguish three typical ablation regimes with different ablation mechanisms. Figure 4 shows effects of different pulse duration ($t_p$) on ablation of a steel foil.

![Figure 4: SEM photograph of a hole drilled in a steel foil with (a) 3.3 ns, 1mJ, $\phi = 4.2$ J cm$^{-1}$; (b) 80 ps, 900µJ, $\phi = 3.7$ J cm$^{-1}$; and (c) 200 fs, 120 µJ, $\phi = 0.5$ J cm$^{-1}$ laser pulses at 780 nm [12].](image)

### 3.4.1 Femtosecond laser ablation

Processing with ultrashort laser pulses ($t_p \ll t_e \ll t_t$) has many advantages over longer pulsed lasers. Using ultrashort laser pulses causes direct solid-vapor or solid-plasma transition at high enough intensities. During the pulse, thermal conduction into the sample can be neglected. When a femtosecond laser pulse interacts with a solid sample, different electronic mechanisms are excited, depending on the sample material [1, 2]. For conducting samples, free electrons inside the solid can directly absorb laser energy and form a hot electron-hole plasma. For semiconductor and wide bandgap dielectrics, the electron-hole plasma is created through nonlinear processes such as multiphoton absorption and ionization, tunneling, and avalanche ionization. At high energy, the electron-hole plasma created on the surface of the solid will induce emission of x-rays, hot electrons, photoemission, and produce highly charged ions through a phenomenon called Coulomb explosion [1, 5, 13].

For wide bandgap dielectrics and semiconductors, where the photon energy is less than bandgap, free carriers are generated due to multiphoton ionization. In multiphoton ionization, $n$ photons are absorbed simultaneously. The simultaneous absorption of multiple photons results in a photoionization rate that is strongly dependent on the laser intensity. The rate of multiphoton absorption [10] can be expressed as

$$\Lambda_{(n)} = \sigma_{(n)} I^n$$

where $I$ is the laser intensity and $\sigma_{(n)}$ is the $n$-photon absorption cross section. Multiphoton ionization contributes to free-carrier generation only for small $n$, since the cross sections become very small for larger $n$. The number of photons required for ionization is determined by the smallest $n$ that satisfied the relation

$$n \omega h = E_g$$

where $\hbar \omega$ is the photon energy and $E_g$ is the bandgap or ionization energy.
For semiconductor samples, where the photon energy is larger than bandgap, single photon absorption is the dominant mechanism for exciting valence electrons to the conduction band. *Tunneling ionization* may come in play under extremely strong laser electromagnetic field interaction with dielectrics. The superposition of the nuclear Coulomb field and the strong laser electric field results in an oscillating finite potential barrier. The bound electrons can tunnel through this reduced potential, thus escaping the atom. In dielectrics, this mechanism allows valence electrons to tunnel to the conduction band in a time period shorter than the pulse duration.

Once electron-hole plasma is formed inside the solid, the carriers can absorb laser photons in a process called *inverse Bremsstrahlung*. Photon absorption increases the carrier energy. When the energy of carriers is well above the bandgap (or Fermi level in a metal), *impact (collisional) ionization* generates additional excited carriers. A high energy electron can ionize another electron from the valence band, resulting in two excited electrons with lower energy at the conduction band. These electrons can be heated by the laser through absorption and impact additional valence electrons. This process can repeat itself and high electron densities can be generated. This process is called *electronic avalanche*. Because of the high electron densities, even originally transparent materials can become strongly absorbing. As a consequence, *optical (or dielectric) breakdown* and plasma formation is often observed. The excitation processes are schematically represented in Figure 5.

**Figure 5:** Interplay of photoionization, inverse Bremsstrahlung, and impact ionization in the process of free carrier plasma formation [14]

**Non-thermal laser ablation**

Laser pulse duration in this regime is shorter than the electron cooling time. Within the femtosecond timescale, a large number of excited electrons can leave the solid. The irradiated solid consist of charged ions and electron-hole plasma but the lattice modes remains vibrationally cold. After about 10% of the valence electrons are removed, the lattice is weakened [5, 8]. Photoexcitation can thus give the atoms and ions enhanced mobility without increasing their thermal energy. When ions gain high enough energy they can break the weakened lattice bonds. They break off instantly without having time to transfer their energy to their neighboring lattice ions. The direct solid-vapor or solid-plasma transition occurs. That process is called Coulomb explosion and is a ‘cold’ alternative to thermal ablation [5, 3]. For non-thermal ablation to be possible, two conditions must be met: ultra-short pulse duration and high enough pulse energy. By depositing the laser energy into the electrons of the material on timescale short compared with the transfer time, the ablation efficiency is improved and ablation threshold is reduced. Heat conduction into the target can be neglected and the heat affected zone is greatly reduced. The fact that the molten layer is practically absent also reduces shock and thermal stress.
Another advantage is the absence of plasma shielding effect because the pulses are so short. Various physical phenomena that can occur when using ultra-short laser pulses are schematically presented in Figure 6. An example of a hole drilled with femtosecond laser pulse is shown in Figure 4c.

Figure 6: Non-thermal ablation and various physical phenomena that can occur when using short pulses [15].

3.4.2 Picosecond laser ablation
For picosecond laser pulse duration (\( t_1 > t_p \gg t_e \)), the sample could be ablated through thermal and/or non-thermal processes, depending on the laser irradiance. In this case, laser ablation is accompanied by electron heat conduction and formation of a melted zone in the target. Hole drilled with picosecond laser pulse is shown in Figure 4b. Electrons are ejected from the target surface during laser pulse. The free electrons can interact with the air and absorb laser energy to initiate an air plasma during the ps laser pulse duration. The plasma forms long before the plume forms. The air plasma above the sample would absorb a part of the incoming laser beam radiation. Unlike ns laser ablation, plasma shielding is not caused by absorption the vapor plume. On the picoseconds time scale, plasma shielding is caused by the air plasma [5].

3.4.3 Nanosecond laser ablation
When the pulse duration is on the order of a few nanoseconds (\( t_p \gg t_1 \gg t_e \)) and laser intensity is on the order of \( 10^7 - 10^{11} \text{ W/cm}^2 \), some mechanisms involved in ablation are: melting, sublimation, vaporization, ionization, etc. If the laser irradiance is high enough, non-thermal ablation is also important and can co-exist with these thermal mechanisms. When the laser irradiance is less than \( 10^7 \text{ W/cm}^2 \), thermal processes are dominant. The temperature distribution in the target can be calculated using equation (10). The temperature at the target surface will rise during the laser pulse and a well defined phase transition occurs; from solid to liquid, liquid to vapor, and vapor to plasma. The whole process is known as thermal ablation.

Thermal laser ablation
This model assumes that excess of the energy of the excited electrons relaxes within the excitation pulse. Because thermalization of the absorbed laser energy takes only a few picoseconds, the thermal model works well for any material that is excited with laser pulses of nanosecond or longer duration. During the nanosecond laser ablation plasma shielding will attenuate the laser beam. The situation becomes more complicated, when stress-related effects contribute significantly to the overall ablation rate. The existence of melting layer makes precise material removal using laser pulses above
nanosecond very complicated. Figure 7 shows various physical phenomena present when machining with long laser pulses.

![Thermal ablation](image)

**Fig 7**: Thermal ablation: various physical phenomena that can occur when using long pulses [15].

### 3.5 Ablation rate

The efficiency of material removal under the action of the laser light is described by the ablation rate. This is defined as ablated depth or volume per laser pulse and is usually expressed as [μm pulse] or [μm³ pulse]. Ablation rate depends on laser (photon energy, fluence, pulse length, width of the laser focus, etc.) and material (the heat and optical penetration depth, internal stresses, etc.) properties and on the type and pressure of the ambient atmosphere. If incubations effects become important or deep holes are fabricated, ablation rate becomes dependent also on the number of pulses. It must be pointed out that effect of individual parameters on ablation rate is difficult to quantify, because they can not be treated independently.

#### 3.5.1 Dependence on laser pulse energy and pulse duration

The effect of the laser energy or pulse duration alone is difficult to quantify. In general, the ablated mass and the ablation rate increases with increase of the laser energy [2,16,17] as shown in Figure 8.

![Figure 8](image)

**Figure 8**: (a) Ablated volume versus energy fluence for different pulse duration [16], (b) ablated depth versus energy fluence for various intensities [17].
When operating with longer pulses, the loss of energy by heat conduction results in lower ablation rates. For nanosecond or longer laser pulses, ablation rate also decreases due to plasma shielding. From Figure 8, it is evident that shorter pulses or higher intensities result in a reduction of the ablation threshold. Although this effect is not fully understood, there are two reasonable explanations. First, with shorter pulses, the spatial dissipation of the laser energy is reduced. Second, for high intensities, the absorption coefficient increases due to multiphoton excitations.

3.5.2 Dependence on spot size
Laser ablation rate also depends on laser spot size. Spot size can be changed by employing different lenses with different focus length or by moving the substrate away from focus. Increasing the spot size reduces the fluence and intensity which results in a reduction of the ablation rate. However, if we keep fluence constant, the ablation rate decreases with increasing spot size when operating with longer laser pulses. When using nanosecond laser pulses, plasma plume can develop during the pulse, and plasma shielding will attenuate the laser beam. With decreasing spot size, the transport of the ablated material becomes effective, and the attenuation of the laser beam decreases. During picosecond or femtosecond pulse, almost no plasma plume can develop and plasma shielding is reduced or even avoided.

3.5.3 Dependence on pulse number
At low number of pulses, some linear dependence of ablation rate on pulse number was observed \([2,16,18]\), as shown in Figure 9.

![Figure 9: Ablation depth versus pulse number for different pulse duration at \(\phi = 6.2 J/cm^2\) [16].](image)

However, as the hole grows deeper upon continued irradiation, it usually narrows below the surface (Figure 10a) [19]. In this case, it is better to define ablation rate as \(\text{ablated volume per laser pulse} [\mu m^3\ pulse]\) instead of \(\text{ablated depth per laser pulse} [\mu m\ pulse]\). Either way, the ablation rate may drastically decrease with high number of pulses (Figure 10b). This is due to various effects. With increasing hole depth, the ablation surface moves away from the focus position and the laser fluence decreases. As the hole grows deeper, the loss of energy by heat conduction increases. The transport of the ablated material becomes less effective and the attenuation of the laser light becomes important. With deep holes, the material recondensation with the hole may appear.

As mentioned, the hole is usually narrowing below the surface, rather than being wider as one might expect from the beam’s diffraction angle. This is because the laser fluence decreases with increasing hole depth. Second reason is nonlinear optical effect called \textit{self-focusing} [1]. This effect keeps the beam...
power concentrated near the axis of the hole and enables deep hole drilling. The self-focusing distance varies with wavelength and peak laser power and therefore must be carefully taken into account.

![Image](image1.png)

Fig. 10: (a) Hole machined with nanosecond laser pulses in glass. (b) Ablated volume versus number of pulses for the hole shown on the left. Hole was drilled at the Faculty of Mechanical Engineering in Ljubljana.

### 3.5.4 Dependence on an ambient atmosphere

A non-reactive atmosphere may also influence the transport of the ablated material and the attenuation of the laser light. Due to collision with gas molecules, the transport of ablated material is hindered with the respect to free expansion in vacuum. Figure 11 shows that the ablation rate increases with decreasing pressure. The ablation rate also increases with decreasing atomic weight of the gas $[2, 20]$.

![Image](image2.png)

Fig. 11: Ablation rate versus laser fluence: (a) air at different air pressure, (b) various atmospheres at 1 bar $[20]$.

### 4 Applications

The removal of material from solid surfaces by the technique of laser ablation has become increasingly important in a variety of applications such as advanced micromachining, mass and emission spectrometry, and fundamental physics studies. In fact laser ablation is now a well-established
technique for the deposition of a wide range of materials in thin film form. Laser ablation is also used in surface cleaning and impressing results were achieved in the restoration of paintings using laser ablation technique (Figure 12).

Fig. 12: Surface cleaning of art; (left) partially and fully cleaned (right). The ablation depth per pulse is about 1\(\mu m\). The process can be monitored by real time spectroscopy of the laser induced plasma which allows precise control of the ablation depth and identification of the different layers [21].

4.1 Laser micromachining

Laser micro-machining is a technology that has developed rapidly over the last years and being applied across many industries. Most widely known industry sectors and manufacturing applications are listed in Table 1. It is impossible to present or describe all of the laser micromachining application and therefore only few examples are shown in the Figures 13, 14 and 15.

<table>
<thead>
<tr>
<th>Industry sectors</th>
<th>Manufacturing applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Semiconductor</td>
<td>- Inkjet printer nozzles</td>
</tr>
<tr>
<td>- Automotive</td>
<td>- Fuel injections nozzles</td>
</tr>
<tr>
<td>- Aerospace</td>
<td>- Microvias in printed circuit boards</td>
</tr>
<tr>
<td>- Electrooptics</td>
<td>- Optical switch tab</td>
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<tr>
<td>- Photonics</td>
<td>- Test probe cards</td>
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<tr>
<td>- Medical</td>
<td>- Chemical sensors (gas flow)</td>
</tr>
<tr>
<td>- Food</td>
<td>- Leak detection</td>
</tr>
<tr>
<td>- etc.</td>
<td>- Microfluidic devices</td>
</tr>
</tbody>
</table>

- Engine silencing
- Food packaging
- Particulate filters
- Solar cell technology
- Turbine blade cooling
- Aerosol atomizers
- Biomedical sensors
- Drug delivery system

Table 1: Overview of industry sectors and manufacturing applications [1, 2, 4, 5, 21, 22, 23]

Fig. 13: Example of ink-jet printer nozzles. (a) Conventional printer nozzle [21]. (b) Array of nozzles with nonlinear tapers to aid the laminar flow of the droplet. (c) Rifled tapered nozzle that spins the droplet to aid its accuracy [22].
Laser micromachining in medicine. (a) Catheter for monitoring blood in prematurely born babies [22]; (b) tungsten pin with reservoir (100\(\mu\)m \(\times\) 1000\(\mu\)m) and capillary (15\(\mu\)m \(\times\) 600\(\mu\)m) used in DNA micro-array machine [23]; (c) Coronary stent for arteriosclerosis treatment [21].

Fig. 15: (a) Printed circuit board (PCB) with laser drilled micro-vias. (b) Laser scribing on thin films for TFS (thin-film silicon) solar cell production [22].

4.2 Chemical analysis

Laser ablation is used in chemical analysis as a method of direct and non-destructive sample introduction [1, 2, 5]. A high-power, short-pulsed laser is focused onto sample surface and vaporizes small volume of the sample. The vapor is then analyzed by measuring atomic or ionic spectra in the induced plasma (LIBS – laser induced breakdown spectroscopy) or by transporting the vapor to secondary excitation source for analysis (ICPS – inductively coupled plasma spectroscopy) [24]. Sample removal is governed by photon-initiated process; therefore, any sample (conducting, non-conducting, organic, inorganic, biological, radioactive, etc.) can be placed in the path of the laser beam. Furthermore, any matter irrespective of its physical state can be (in principle) analyzed. There are no sample size requirements and no sample preparations. This eliminates chemical solvents (and waste) which are used in standard chemical analysis methods. Another advantage is the ability to depth profile the sample by repeatedly ablating the same position. This can also be used for the removal of the surface contamination before analyzing the sample.

The most widely used approach is laser induced breakdown spectroscopy (LIBS). LIBS is a method for fast and in-site quantitative elemental analysis of any sample irrespective of its physical state (solid, liquid or gaseous). Since LIBS requires only optical access to the sample it can be employed for remote analyses. This is ideal for use in hazardous environments (radioactive or poison contamination) or in space explorations. Being practically non-destructive and non-invasive technique it is also ideal for the analysis of the art work and archeological artefacts. Major disadvantages are limited reproducibility and sensitivity.
4.3 Pulsed Laser Deposition (PLD)

The widespread use of laser ablation for thin-film deposition, referred as pulsed laser deposition (PLD), has experienced an enormous growth. The list of materials that have been grown using PLD technique includes such diverse items as optical coatings, compound semiconductors, high temperature superconductors, diamond-like carbon (DLC), ferroelectrics and bioceramics [1, 3, 4].

From the conceptual point of view, the LPD technique is very simple and only requires a pulsed laser, a target and a substrate. The basic setup of the conventional configuration has been sketched in Figure 16. The ablation of the material is generally performed by a nanosecond excimer laser, operating at UV wavelengths (248 and 193 nm). These wavelengths are weakly absorbed by the plasma, which minimizes plasma influence on the ablation process. One of the advantages of PLD is that the process can be performed at any pressure ranging from ultra high vacuum to high pressure (typically up to 10mb ar) and any kind of atmosphere either inert or reactive can be used. Another advantage of PLD is its flexibility to use several targets in a single film growth process. The laser beam can easily be focused alternatively to two or more targets, leading to a sequential ablation process. This configuration (referred as alternate PLD or a-PLD) is ideal for producing complex structures such a multilayers or nanostructured films.

![Diagram of PLD experimental setup](image)

Fig. 16: Schematics of standard PLD experimental setup. The laser beam is focused to the target typically at angle of incidence of 45°. Target is typically rotated to keep its surface under approximately constant conditions [25].

5 Conclusion

Basic physical principles of pulsed laser ablation were presented. Detailed physical mechanisms are not entirely explained and are subject of further studies. Among those, not fully explained mechanisms, are plasma-sample and plasma-laser beam interaction, detailed non-thermal ablation mechanism, etc. Regardless of detailed mechanisms, many important applications depend on laser ablation. In this seminar only most widely used application were presented; laser micromachining, chemical analysis and pulsed laser deposition.
References


