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# Ablation of solids by Femtosecond Lasers: Potential applications

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**Abstract:** Recent years have witnessed a rapid expansion of research on nanofabrication technologies towards tailoring artificial materials with desired nanostructures. Bottom-up approaches, focusing on weak and reversible non-covalent interactions between molecules seek to have small, usually at molecular level, components built up into complex assemblies, while top-down approaches aim at creating nanoscale devices from bulky materials. Although bottom-up approaches are feasible to produce two and three dimensional structures at low cost, it still could not accommodate the increasing demand of structural complexity. Given that appropriate parallel processing strategies are discovered, a top-down technology may find broader usage in manufacturing structurally complex and functionally advanced devices. Laser modification of semiconductors has been an area of intensive applied and fundamental research for over three decades. Research has been partially motivated by the possibility of laser applications in processing of semiconductors, especially in the electronics and optoelectronics industries. Laser ablation is the removal of materials from a substrate by direct absorption of laser energy, which can produce the desired combination of narrow and clean patterning because of their advantage in localized heating and material removal. The mechanism of ablation of solids by intense femtosecond laser pulses is described in an explicit analytical form. It is shown that at high intensities when the ionization of the target material is complete before the end of the pulse, the ablation mechanism is the same for both metals and dielectrics. The physics of this new ablation regime involves ion acceleration in the electrostatic field caused by charge separation created by energetic electrons escaping from the target. This paper deals with the detailed study of femtosecond laser pulses, interaction between laser radiation and solid state laser ablation, comparison of nano and femtosecond laser ablation and their applications.

**Keywords**: Femtosecond laser, Nanosecond laser, Pulses, Ablation, Interaction and Applications.

## INTRODUCTION

The unique electronic, optical and catalytic properties of noble-metal nanoparticles and nano structures have attracted increasing interest in recent years. Nanoparticles and nano structures can be fabricated by a large range of different techniques including directly laser ablation, laser induced forward transfer, laser induced backward transfer, laser-induced self-assembly and chemical reduction[1-5.] Of these methods, directly laser ablation is a highly efficient method for fabricating nano particles and nano structures. Over the past decade, pulsed laser ablation in liquid (PLAL) has gained intensive attention for its widely used in the synthesis of nanomaterials. Remarkably, a large variety of nanomaterials such as metals, metallic alloys, metal oxides, semiconductors and carbon-related materials have been synthesized by PLAL[6]. While the study on the fundamental mechanism of PLAL, especially for femtosecond laser ablation, is far from enough and only a relatively general description has been given. Therefore, greater research efforts are still required to obtain in depth and thorough understanding of femtosecond laser ablation[7].

Atomic emission and atomic mass spectrometry are powerful tools for rapid element analysis. Nowadays in particular the inductively coupled plasma (ICP)-based spectrometry, e.g. inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES), have become routine analytical methods for many applications, such as analyses of biological and environmental samples, elemental determinations in metals and alloys, analyses of glasses and other hard materials[8]. The tremendous success of these techniques is based on the distinguished capability of the ICP as the excitation and ionization source. When aerosol or gas samples pass through the plasma, a series of processes such as vaporization, atomization and ionization occur in sequence to generate large quantities of atoms and ions for analyses. Usually, gases and liquid samples are easy to be introduced to the ICP. However, for solid samples, this is not always true, which limits the applicability of ICP-MS and ICP-OES for elemental analysis of solid materials[9,10].

Laser ablation has become a very versatile technique for direct in situ solid sampling since the first tests in 1985. It is nowadays widely used in different industrial and scientific fields associated with material science and more recently with earth sciences. In that case, the laser ablation system is often coupled to a mass spectrometer in order to directly measure chemical or isotope composition of natural geological samples. The first systems used infrared (IR) laser beam ($\lambda$ = 1064 nm), providing nanosecond pulses, but they had no useful outcomes for highly transparent, IR transmitting, material such as quartz, mostly because of catastrophic ablation. Unfortunately, a lot of common geological studies involve transparent materials like quartz, fluorite or calcite. For fluid-inclusions studies, the ablation problem has been solved by using laser sources directly producing fundamental wavelength (Ar:F, 193 nm). They are commonly used in the earth sciences for Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) studies of geological materials. In the same time, laser devices producing femtosecond pulses have been developed. They greatly reduce thermal effects and chemical fractionation during ablation compared to nanosecond lasers in LA-ICP- MS. This is mainly due to ablation mechanism in the femtosecond regime which is deeply different from nanosecond regime. Photomechanical rather than thermal processes are involved, which are potentially able to ablate any kind of geological material, independently from the transmittivity of the laser wavelength[11].

The rapid development of femtosecond lasers over the last decade has opened up a wide range of new applications in industry, material science and medicine. One important physical effect is material removal or laser ablation by femtosecond pulses which can be used for the deposition of thin films; the creation of new materials; for micro-machining; and in the arts, for picture restoration and cleaning. Femtosecond laser ablation has the important advantage in such applications compared with ablation using nanosecond pulses because there is little or no collateral damage due to shock waves and heat conduction produced in the material being processed. In order to choose the optimal laser and target parameter it is useful to have simple scaling relations, which predict the ablation condition for an arbitrary material[12].

## ABLATION MECHANISM

Though dielectric materials do not normally conduct a current, they can be forced to conduct under the right conditions. This change in the material's properties and behavior is called a breakdown and can lead to material damage, a permanent change in material properties, or the removal of material. Lasers may utilize this material breakdown by targeting a sample with a laser's output of appropriate wavelength and temporal duration. When using lasers, the breakdown is due to the interaction of the material with the light radiation and is called optical breakdown. High laser pulse intensities focused onto incredibly small areas can create the electric field strength required to cause ionization. When irradiating the sample material, the laser pulse transfers its energy to the electrons through a nonlinear photoionization method. The free electrons are produced by one of the nonlinear photoionization methods of tunneling ionization, multi-photon ionization or a combination of both of these. Any free electrons produced by tunneling escape with the aid of the laser radiation due to the resulting suppression of the electric field strength that binds the electrons to the valence band[13]. Free electrons produced by multi-photon ionization simultaneously absorb energy from several separate photons to overcome the binding electric field strength. Regardless of the mechanism producing the free electrons, these electrons gain kinetic energy within the laser's electric field and can collide with bound electrons. If enough energy is transferred during the collision, the bound electrons will be freed. This process is called impact ionization and will continue to exponentially create more free electrons through multiple iterations in a process called avalanche ionization.

Once enough free electrons are produced, the section of the material targeted by the laser behaves like plasma; it responds to electric fields and has a very high electrical conductivity. Once the free electron density reaches the critical value of $10^{22}$ $cm^{-3}$ to $10^{23}$ $cm^{-3}$, the electrons behave as plasma that has a natural frequency of oscillation that resonates with the laser and efficiently absorbs and reflects the laser pulse energy. Coulomb repulsion between like charges causes a quick expansion of the local plasma in the form of a plume. This rapid expansion resembles an explosion and a shock wave is created within nanoseconds of irradiation. The plasma expansion may be visible as a spark and the shock wave may be audible. The final results of laser-induced optical breakdown may include permanent material damage, altered material properties such as the index of refraction or even the removal of material known as ablation[14].

**Interaction between laser radiation and solid state laser ablation:** Laser ablation of solid states generally implies the conversion of optical into thermal energy via electronic excitation, followed by the vaporization and ejection of species from the irradiated volume. In fact, laser radiation can effectively interact only with electrons located in the conduction band of a solid state. Therefore, the mechanisms of energy absorption are supposed to vary strongly for dielectric and metallic materials. Regarding metals or semiconductors the laser energy can directly be absorbed by the process of inverse Bremsstahlung because of their large initial number of free electrons[15]. However, energy deposition in wide-band-gap materials requires the build-up of a certain density of seed electrons inside the conduction band since its thermal population is usually too small. If the photon energy is less than the band gap, electronic inter-band transitions must be induced via a non-resonant multi-photon absorption (MPA) and avalanche ionization (AI)[16-18]. If a sufficient number of free electrons are present, the incoming pulse energy can efficiently be absorbed by inverse Bremsstrahlung to transient temperatures of around 104 K. Corresponding heating rates are approximately $10^{14}$ K/s. Thus, electron heating is accomplished within a few hundreds of femtoseconds, as indicated in **Fig.1**. However, the subsequent energy transfer to the lattice is more time-consuming. The lattice heating, which is controlled by the strength of the electron-phonon coupling, happens on a timescale ranging from a few up to several tens of picoseconds, depending on the material considered[19].

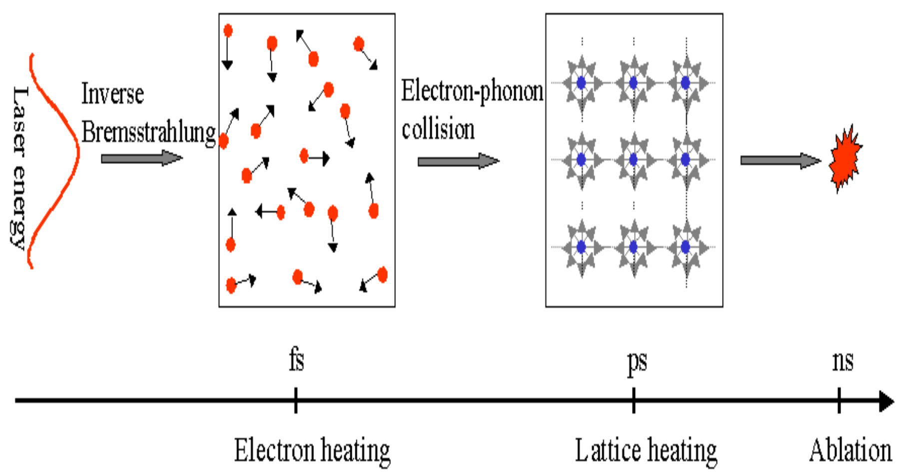


**Fig.1:** Energy transfer process from optical to thermal energy on a timescale ranging from femtosecond to nanosecond duration

In case of nanosecond laser ablation, the pulse duration is by far larger than the lattice heating time. Therefore, the laser-solid interaction is of adequate time to deposit energy not only in the irradiated zone, but also in its neighboring volume due to strong thermal diffusion. The corresponding heat penetration depth depends on the heat diffusion coefficient of the material and the pulse[20] duration (τ). For pico or femtosecond laser pulses, τ usually falls below the electron cooling time. Phonon excitation due to electron-phonon coupling and subsequent solid-liquid phase transitions is therefore confined to the irradiated zone. The perimeter of zone heating in this limiting case is determined by electron diffusion that is on the order of 100 nm. Heat transfer as a result of phonon migration out of volume can completely be neglected. Nevertheless, inside the irradiated volume, electron-phonon coupling eventually results in the decomposition of the lattice structure as the material-specific critical point has been reached and material ejection takes place

Quantitatively, the interaction of ultra-short laser pulses with solid states can be described by the two-temperature model which treats the heat conduction for electrons and lattice separately[21]. First, the laser energy is absorbed by free electrons, which brings an immediate temperature rise, while the lattice still remains at ambient temperature. Then, the energy is delivered to the lattice because of the temperature gradient. After that, both electron and lattice temperatures equilibrate. A schematic diagram is given in **Fig.2** showing the processes of laser-matter interaction for femtosecond ablation[22].

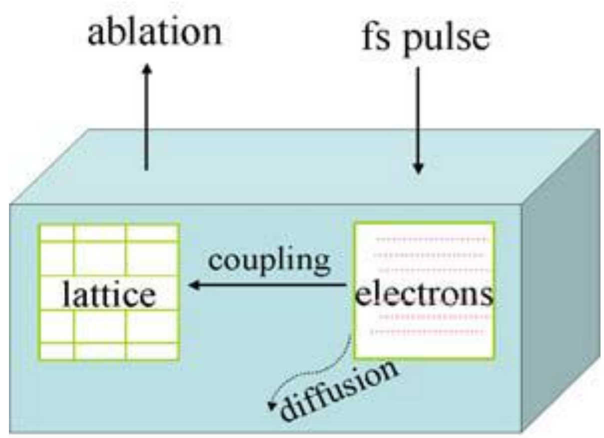


**Fig.2:** Schematic diagram of the laser-matter interaction using femtosecond pulses

## COMPARISON OF NANO AND FEMTOSECOND LASER ABLATION

Most applications of laser ablation have been done with nanosecond lasers. However, nanosecond lasers have been found to form the so-called heat-affect zones which are caused by thermal diffusion into the target. Consequently, elemental fractionation due to fractional evaporation and material redistribution can occur even if the local temperature is high enough to evaporate the most refractory elements. Moreover, a part of the pulse energy is dissipated above the exposed area that, in turn, may affect the composition of aerosol particles formed during material expansion. Zone heating and plasma shielding are obviously both related to the pulse duration, which governs the ablation process[23]. In contrast, femtosecond lasers show great advantages over nanosecond lasers in interaction with solid materials. Furthermore, stoichiometric aerosols are ablated[24]. This significantly improves the analysis performance of an ICP-based spectrometer.

## APPLICATIONS

Femtosecond laser micromachining has become increasingly important in recent years for many fields, including micro-optics, micro-electronics, micro-biology and micro-chemistry. Laser ablation, because of its non-contact nature, allows the micromachining and surface patterning of materials with minimal mechanical and thermal deformation. It is now well known that for many of these applications, the femtosecond regime offers advantages over the nanosecond regime. These advantages lie in its ability to deposit energy into a material in a very short time period, before thermal diffusion can occur. As a result, the heat-affected zone, where melting and solidification can occur, is significantly reduced. Smaller feature sizes, greater spatial resolution, and better aspect ratios can hence be achieved [25].

Femtosecond Laser Ablation is the process of low threshold material removal from surfaces governed by plasma formed at the surface of the material via generation of hot electron hole pairs excited via multi-photon absorption. Plasma energy is then transferred to the material through the lattice expansion and bond breaking. The thermal diffusion into material is nearly negligible as all processes accompanied femtosecond laser ablation are happening on a pico second time scale and material does not have enough time to melt and re-solidify, consequently better precision of laser micromachining can be achieved. Due to the fact that thermal processes are much less pronounced in the femtosecond laser ablation mechanism, the structured areas formed in material processed, using femtosecond lasers are smooth and without any visible cracks. A very promising application of femtosecond laser beam processing is the three dimensional microstructuring inside UV transparent materials, which can be utilized to create photonic crystals, waveguides, Bragg gratings, etc[26].

Femtosecond lasers have huge potential in the field of micro/nano machining. The ultra short laser pulse properties achieve an unprecedented degree of control in sculpting the desired micro/nanostructures internal to the materials without collateral damage to the surroundings. When laser energy is deposited at a timescale much shorter than both the heat transport and the electron phonon coupling, the light-matter interaction process is essentially frozen in time, minimizing collateral damage to the surroundings. Also, because the machining process is not dependent on the linear absorption at the laser wavelength, virtually any dielectrics, metals and mechanically hard materials can be machined by the same laser beam[27]].

## CONCLUSIONS

Over the past decade, pulsed laser ablation in liquid has gained intensive attention for its widely used in the synthesis of nanomaterials. Remarkably, a large variety of nanomaterials such as metals, metallic alloys, metal oxides, semiconductors and carbon-related materials have been synthesized by PLAL. The rapid development of femtosecond lasers over the last decade has opened up a wide range of new applications in industry, material science and medicine. One important physical effect is material removal or laser ablation by femtosecond pulses which can be used for the deposition of thin films; the creation of new materials; for micro-machining; and in the arts, for picture restoration and cleaning. Femtosecond Laser Ablation is the process of low threshold material removal from surfaces governed by plasma formed at the surface of the material via generation of hot electron hole pairs excited via multi-photon absorption. Plasma energy is then transferred to the material through the lattice expansion and bond breaking.

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