Vibration assisted femtosecond laser Invar36 hole drilling processing and Ag nano-particle synthesis by laser ablation in liquid

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초록

재료 및 펨토초 펄스 레이저 상호 작용은 재료 과학 분야뿐만 아니라 실제 응용 분야에서도 중요하다. Solid-state 레이저와 Ti:sapphire 레이저를 사용하는 처프 펄스 증폭 기술의 발전으로 기존 기술로 높은 인텐시티를 만들어내기 어려운 문제가 해결되었다. 펨토초 레이저 응용 분야에는 고강도 물리학, 펨토초 펄스 레이저 가공 및 고차 고조파 생성이 있다. 펨토초 레이저 공정은 펨토초 레이저 어플리케이션에서 가장 유망한 기술 중 하나이다. 이것은 가공 메커니즘이 기존의 나노초 및 CW 레이저 가공과 크게 다르기 때문이다.

본 논문에는, 첫째, 동기와 배경 및 선행 연구를 소개한다. 둘째, 이론적으로 재료-펨토초 펄스 상호 작용 및 공정에 대해 설명한다. 펨토초 레이저에 의한 금속 가공은 이론적으로 two-temperature 모델을 사용하여 설명된다. 펨토초 레이저 가공은 two-temperature 모델에 의해 계산 된 전자 기여도를 고려한 물리학 이론에 의해 표현된다. 가공 시, heat diffusion length와 penetration depth를 이론적으로 계산하였다. 셋째, 진동자를 이용한 펨토초 레이저 홀 가공 공정을 이론적, 실험적으로 설명하였다. 진동을 홀 가공 공정에 적용 할 때, 진동자의 거동이 가공에 미치는 영향을 조사하기 위해 FIB를 통하여 단면 프로파일을 얻었다. 데이터를 추출하여 수치 해석에 적용하고 결과를 계산과 비교하였다. 진동자가 실제로 산업 현장에 적용될 때 발생할 수 있는 진동자와 레이저 간의 동기화 문제를 확인하기 위한 실험이 수행되었다. 이 실험 조건에서 가장 깊은 가공 깊이는 진동자와 레이저가 동기화되었을 때 얻어졌다. 이론적 및 실험적 연구에 따르면 가공 깊이와 테이퍼 각도는 레이저-진동자가 동기화된 조건에서 진동자의 최대 진폭만을 조정하여 조정할 수 있다. 검증을 위해 Invar36 재료에 대해서 진동자의 최대 진폭을 제어하여 테이퍼 각도를 조절한 결과를 데모로 나타내었다. 마지막으로, Ag에 대한 액체 중 레이저 가공에 대해 설명한다. 액체 중 레이저 가공은 (LAL) 계면활성제 없이 다양한 고순도 나노 물질을 합성하는 간단한 기술이다. 그러나, 합성 공정을 제어하는 것이 어렵기 때문에, 합성된 나노 물질은 항상 높은 분산도 (σ)로 넓은 분포를 갖는다. 계면 활성제가 없으면 입자 성장이 발생하여 콜로이드 크기를 조절하기가 어려워진다. 따라서 입자 크기가 중요한 생물학, 촉매 및 광학적 응용 분야에 사용하기 위한 LAL을 통해 합성된 나노 물질의 경우 입자 성장을 억제하면서 콜로이드 크기를 제어하는 전략을 찾는 것이 중요하다. 이것은 콜로이드를 저장하는 동안 입자 성장이 어떻게 일어나는지, 입자가 얼마나 커지는지, 입자의 모양이 어떻게 변하는지에 대한 일련의 질문을 제기한다. 이러한 질문에 답하기 위해 계면 활성제가 없는 아세톤 중 펨토초 레이저 가공을 통해 합성된 Ag 입자 (2-10 nm)를 6 개월 동안 저장하였다. 탄소 캡슐화를 통해 큰 입자와 다각형 입자 (5~50 nm)로 성장하였고, 이 입자들이 자발적 크기 분리 현상을 통해 입자 침강이 발생하는 것을 확인하였다. 따라서 매우 작은 입자 (5 nm 이하)는 콜로

이드에서 가장 높은 비율을 차지한다. 또한, 우리는 동시에 콜로이드 크기를 제어하고 입자 성장을 억제하면서 ex-situ SU-8 기능화를 통해 입체 구조 또는 필름제조에 적용 할 수 있는 방법을 제안한다. 아세톤에서 Ag의 펨토초 레이저 가공을 통해 합성된 Ag 나노 입자는 ex-situ SU-8 기능화를 거쳐 6 개월 동안 저장되었으며, 그 후 10 nm 이상의 대부분의 입자가 응집체 및 침전물이 되었고 콜로이드의 분산도(σ)가 48-78%, 4-5 nm의 평균 직경으로 좁혀졌다. Ag 입자에 대한 SU-8의 라디칼 중합이 자발적인 크기 분리 및 성장 억제의 원인으로 추정된다. 이 연구의 결과는 콜로이드 질량의 절반이 라디칼 중합으로 인한 콜로이드의 침전으로 인해 낭비되긴 하지만, ex-situ SU-8 기능화를 사용하여 LAL을 통해 합성 된 콜로이드의 더 나은 크기 제어를 위한 새로운 방법을 제공 할 것이다.

ABSTRACT

Vibration assisted femtosecond laser Invar36 hole drilling processing and Ag nano-particle synthesis by laser ablation in liquid*

Material and femtosecond pulsed laser interactions are of interest in practical applications as well as material science interests. Advances in chirped pulse amplification techniques using solid-state lasers and Ti:sapphire lasers have solved problems that are difficult to achieve with high intensity. Applications include high-intensity physics, femtosecond pulsed laser processing, and high-order harmonic generation. Femtosecond laser processing is one of the most promising technologies in femtosecond laser applications. This is because processing physics is significantly different from conventional nanoseconds and long pulse laser machining.

In this dissertation, first, this paper introduces motivation, background, and previous research. Second, theoretically describes matter-femtosecond pulse interaction and processing. Machining of metals by femtosecond lasers is theoretically described using a two-temperature model. Femtosecond laser ablation is expressed by a physics theory that takes into account the electron contribution calculated by the two-temperature model. The processing rate and the thickness of the heat affected zone are theoretically estimated. Third, the vibration assisted femtosecond laser hole drilling process is explained experimentally and theoretically. Experiments were conducted to investigate the effects of vibration on the ablation profile when applied to the hole drilling process, and cross-sectional profiles were obtained through FIB. Data were extracted and fitted for numerical analysis, and the results were compared for vibration parameters. Experiments were conducted to investigate the synchronization problem between the vibrator and the laser which may occur when the vibrator is actually applied in industrial field. In this experimental condition, the deepest ablation depth was obtained when the vibrator and laser were synchronized. Theoretical and experimental studies have confirmed that the ablation depth and taper angle can be adjusted by adjusting

only the maximum amplitude of the vibrator under the condition where synchronization is appropriate. For this purpose, the results of adjusting the taper angle by controlling the vibration amplitude of Invar 36 material were shown as a demonstration. Lastly, Laser ablation Silver in liquid results are described. Laser ablation in liquid (LAL) is a simple technique for developing various high-purity nanomaterials without surfactants. However, due to the difficulty of controlling the particle synthesis process, the fabricated nanomaterials always have a large distribution with a high degree of dispersion (σ). The lack of surfactants can also cause problems in particle growth, which makes adjusting colloid size more difficult. Therefore, for nanomaterials synthesized through LAL to be widely used in biological, catalytic, and optical applications in which particle size plays an important role, it is important to seek strategies to control colloid size while also inhibiting particle growth. This raises a series of questions concerning how particle growth occurs in colloid storage, how large the particle grows, and how the shape of the particle changes. To answer these questions, Ag particles synthesized through femtosecond (fs) laser processing of Ag in acetone were used as starting materials, and the Ag particles (2-10 nm) generated through LAL with no surfactants were stored for six months. Through carbon-encapsulation they grew into large particles and polygonal particles (5-50 nm), and the spontaneous size separation phenomenon was found to be induced by particle precipitation. Very small particles (5 nm or less) comprised the highest ratio in the supernatant. In addition, we propose a method to fabricate and gain the ability to apply a three-dimensional structure or film through ex-situ SU-8 functionalization using polymerization, while at the same time controlling colloid size and inhibiting particle growth. The Ag nanoparticles (NPs) synthesized through fs laser processing of Ag in acetone were subject to ex-situ SU-8 functionalization and stored for six months, after which most particles larger than 10 nm became aggregates and precipitates and the size distribution of the supernatant narrowed to an average diameter of 4-5 nm with σ of 48-78%. Radical polymerization of SU-8 for Ag NP is presumed to be the cause of spontaneous size separation and growth inhibition. The results of this study are expected to provide a new method for better size control of colloids synthesized through LAL

using ex-situ SU-8 functionalization, even though half of the colloid mass is wasted due to the precipitation of colloids resulting from radical polymerization.

Keywords: Vibration assisted femtosecond laser processing, Theoretical investigation, Invar36, Laser ablation in liquid, Ag

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Contents

Chapter 1. Introduction

1.1. General characteristics of lasers and femtosecond lasers

Since the invention of the laser in 1960, pulsed-laser machining has been extensively studied. Lasers are used in a vast variety of industrial applications such as cutting, hole drilling, surface treatment, and welding. However, nanoscale laser machining has not yet found many application fields. Laser machining is generally used to form supra-nanostructures. For example, excimer lasers are primarily used for micromachining of ceramics and polymers and crystallizing amorphous indium tin oxide (ITO), and Neodymium-Doped Yttrium Aluminum Garnet (ND:YAG) lasers are typically used for microscale hole drilling, cutting, and marking. Moreover, nanosecond or microsecond lasers can cause thermal or mechanical damage (e.g. melting, formation of burr, and thermal cracking, and morphological change). In various applications for fabricating metallic microstructures, these limitations can be overcome by using ultrashort laser pulses (in the order of picoseconds [10^{-12} s] or femtoseconds [10^{-15} s]), which leave no or negligible heat-affected zone or microcracks on a surface that is being machined owing to extremely short pulse durations, thus minimizing the collateral damage and thermal diffusion of the irradiated surface of the workpiece. For these advantages of ultrashort laser pulses, a great deal of research is underway to apply them in the field of micromachining.

Femtosecond lasers are excellent micromachining tools for fabricating microstructures on practically any solid materials, such as metallic, non-metallic, semi-conductive, transparent, and polymeric materials, with relatively low post-treatment requirements. In particular, femtosecond laser machining offers great potential for applications sensitive to collateral damage because it has extremely low thermal diffusion in the area around the irradiated zone.

Femtosecond laser micromachining is a process of fabricating micro/sub-microscale structures on the surface of an absorptive or transparent material or inside of a

The basic concept of mode-locking is in fact simpler than the explanation given above. It basically involves a simple method of locking other modes competing for the available gain. Prior to the advent of KLM, the following two methods were used as mode-locking techniques: (a) Active mode-locking (using an acousto-optic modulator for frequency modulation to maintain fixed modes) and (b) Passive mode-locking (using a saturable absorber to induce time-dependent loss). The basic principle of mode-locking is to induce the total laser power to be concentrated on a narrow time window within a pulse by eliminating weak magnetic fields and strengthening strong magnetic fields. A large number of lasers are still operating by this mechanism, mostly in the picosecond regime. The main limitation of this approach is the reaction time in active or passive mode-locking, i.e., the time to trigger changes within the cavity.

KLM is a self-locking process. In most cases, all modes are locked automatically without any external intervention such as installing active or passive modulators in the laser cavity. KLM was first observed unexpectedly in a Ti:sapphire oscillator [Spence et al., 1991; Keller et al., 1991]. KLM occurs by the nonlinear optical effect of Ti:sapphire crystal, a process in which the refractive index of Ti:sapphire changes according to the laser intensity of a mode-locked laser, with the refractive index increasing more at the center part than in the periphery due to laser intensity difference, with the crystal acting like a Kerr lens, resulting in the so-called optical Kerr effect of the gain crystal, i.e., an intensity-dependent refractive index variation. The operating regime of a mode-locked short pulse laser can obtain the nonlinear effect more efficiently compared with that of a continuous-wave (CW) or random-phase, multimode laser, resulting in oscillation to generate even shorter beam radii. In this process, ultrashort pulses can be generated by selectively reducing the loss using a variable aperture placed in the cavity. This suggests that stable operation is possible only in the mode-locked state. Spikes in an active or passive cavity transform the laser from CW operation to mode-locking operation (for informative structural and functional diagrams representing various operating regimes of mode-locked lasers, see [Keller, 2003]). Most femtosecond oscillators are Kerr-lens mode-locked lasers. They have a simple cavity because no additional medium is needed, and the effect is immediate. A kerr-lens mode-locked femtosecond laser oscillator can generate ~5 fs pulses [Pshenichnikov et al., 1998]. Since all the optical elements inside a laser cavity trigger nonlinear dispersion, the phase relationship among various wavelength components should be maintained using prisms or chirped mirrors to compensate for the cavity dispersion.

However, a femtosecond oscillator typically operates in the order of a few nanojoules (nJ) per pulse. Machining applications of such ultrashort pulses require multi-stage amplifications to achieve the required intensities. However, early research into ultrashort pulse amplification had some limitations (see, for example, [Köechner 1996]). Besides laser-induced optical loss, serious negative effects arose due to intensity-dependent phase shifts [Perry & Mourou, 1994]. Furthermore, beam radius expansion aiming to reduce the pulse intensity is cost-intensive because of larger system size requirement. This limitation was overcome by an ingenious concept of chirped pulse amplification (CPA) [Strickland & Mourou, 1985; Maine et al., 1988]. Figure 1.2.1 illustrates the mechanism of CPA.

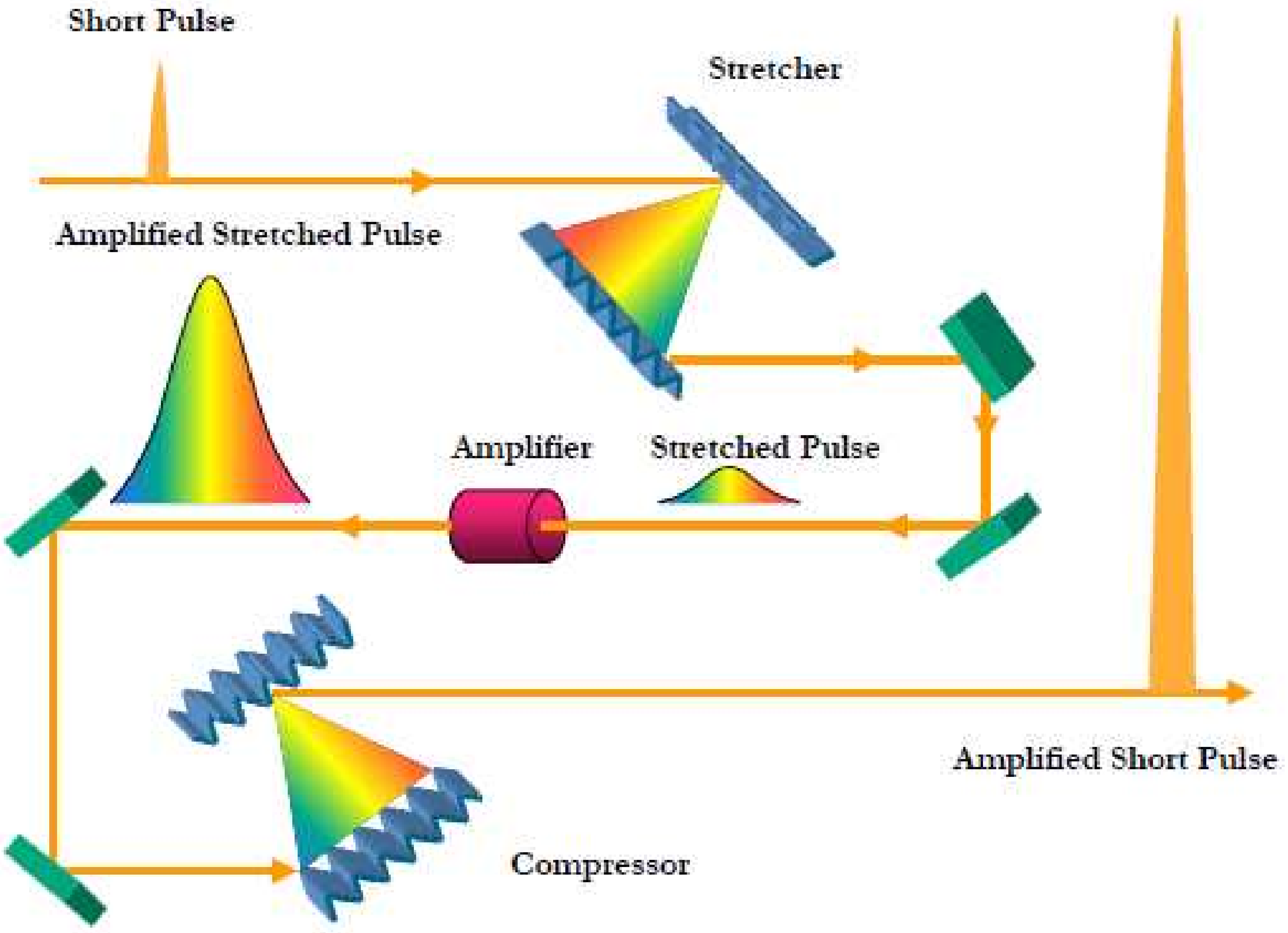

Figure 1.2.1. Schematic diagram of a Chirped Pulse Amplifier system. [Mourou & Umstadter, 2002]

The CPA technique uses a laser pulse stretcher (grating/mirror combination in the system) to increase the low energy femtosecond pulse generated by the oscillator along the time axis [Pessot et al., 1987]. The stretcher gives rise to a phase shift in all the frequency components of a pulse. Chirp is defined as an instantaneous frequency with time-dependent phase shift of a pulse caused by phase modulation in a femtosecond pulse system. Given that a stretched pulse is associated with phase mismatch of frequency elements, when selecting a stretcher, care should be taken to avoid a loss of the pulse bandwidth. In general, a pulse is amplified by a regenerative-multipath amplifier system. The intensity of a stretched pulse should be maintained at a level low enough not to trigger nonlinear effect of the optical elements of the amplifier. Ideally, an amplified pulse is recompressed to the original pulse width using a grating compressor [Pessot et al., 1987; [Strickland & Mourou, 1985]. However, the pulse compression is limited by the gain narrowing that occurs in the final amplifier stage [Siegman, 1986; Perry et al., 1990] and the residual uncompensated dispersion of the pulse added during the course of amplification. To overcome this limitation and ensure efficient compression to the original pulse duration, two or more compressors are needed. Despite these limitations, however, CPA is currently the standard technique for high-power femtosecond laser systems.

1.3. Typical femtosecond laser machining tools, systems, and setup

Most femtosecond lasers for micromachining applications use Ti:sapphire as the gain medium. In general, a Ti:sapphire laser oscillator has a megahertz repetition rate, pulse width ranging from 50-100 fs, and pulse energy of several tens of nanojoules. Although there are high-energy laser oscillators as well, it is essential to amplify the laser oscillator output to obtain pulse energies greater than microjoules, whereby the repetition rate is reduced to the order of kilohertz.

Micromachining of a transparent material required a femtosecond laser oscillator or amplified femtosecond laser system. In both cases, the laser beam is focused on the sample using an objective lens. When performing micromachining using a laser oscillator with nanojoule pulse energy, a microscope objective with higher numerical aperture (NA) is necessary to ensure intensities suitable for the intended machining. An amplified laser system generates much higher energy than a laser oscillator. That is, an objective with lower NA can be used to obtain the same intensities. In a typical micromachining setup for a transparent material, the microscope objective is held fixed and the sample is placed on a movable 3-axis stage. The sample stage moves along the laser beam emitted at the set pulse repetition rate and continuous structures are fabricated on the sample surface or inside the material.

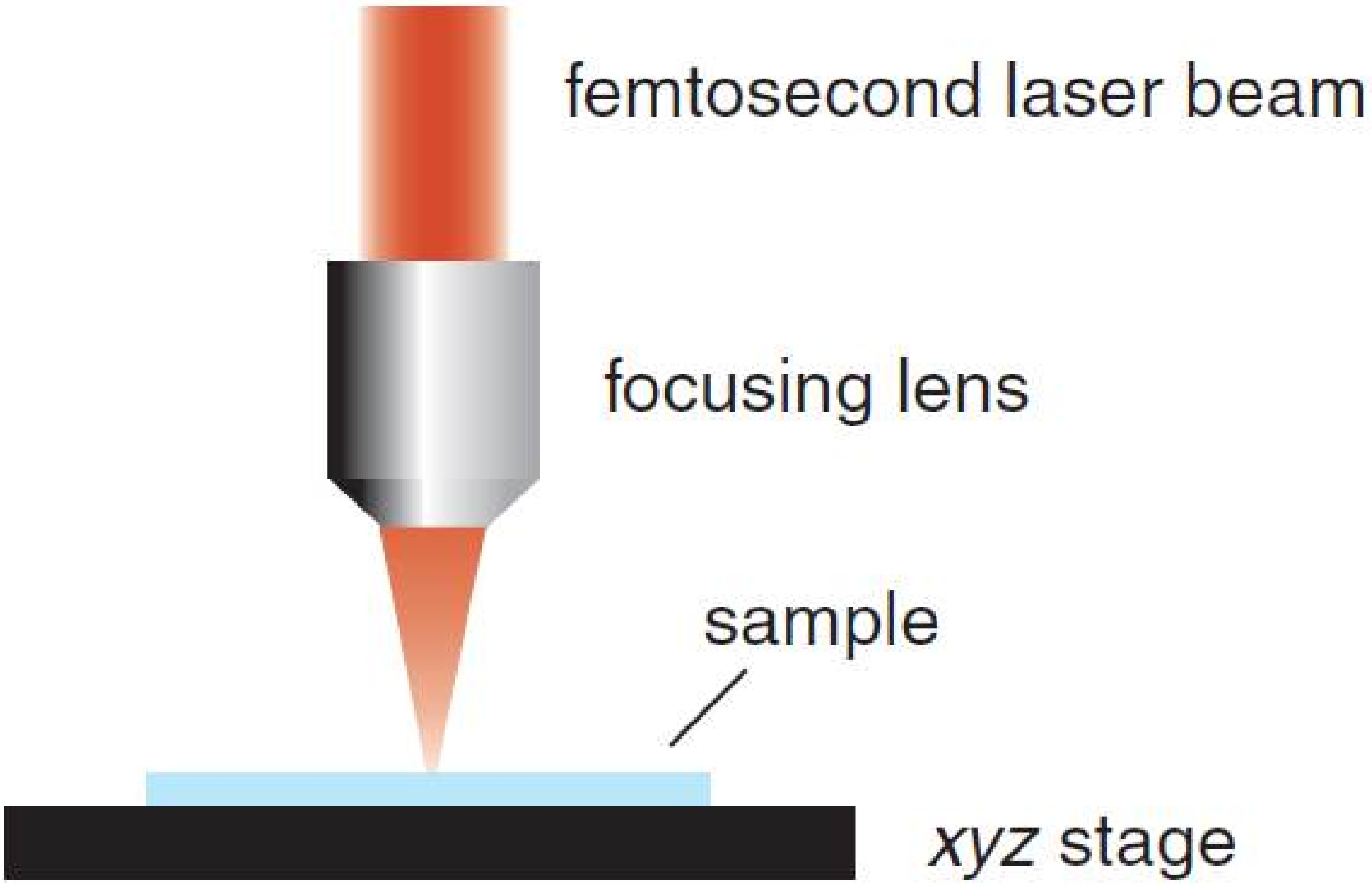

Figure 1.3.1. Schematic diagram of typical micromachining setup. A femtosecond duration laser pulse is tightly focused by a microscope objective or lens onto the surface of an absorbing or transparent material for ablation or into the inside of a transparent sample for bulk micromachining. The sample is mounted on a three-axis translation stage and its position is scanned relative to the laser focus to produce the desired microstructure. [J.K. Park, 2012]

A typical micromachining setup for an absorptive material is similar to that for a transparent material, whereby a microscope objective is used for focusing the laser beam onto the sample surface. For applications requiring larger structures such as hole drilling, long focal length lenses are often used. Although different aspects may come into play in laser–material interaction, the basic mechanisms for micromachining transparent and absorptive materials are essentially the same.

Laser parameters and material properties greatly influence the laser–material interaction and micromachining performance. Pulse energy, repetition rate, wavelength, and pulse width are some of the laser parameters essential for the laser pulse absorption by solid materials. Material properties, such as band gap and thermal properties, determine the feasibility and performance of micromachining with femtosecond pulses. The process of laser energy absorption by target material and the mechanism of laser–material interaction are the key to understanding the micromachining process.

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