Femtosecond laser based high-performance micro-hole drilling on metal with vibration assistance and AgNW/CNT hybrid film patterning

Ji-Wook Yoon

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Supervisor Sung-Hak Cho

We hereby approve the Ph.D. thesis of "Femtosecond laser based high-performance micro-hole drilling on metal with vibration assistance and AgNW/CNT hybrid film patterning".

May 2015

sign _____

Chairman of Thesis Committee

sign _____

Thesis Committee Member

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먼저 학위과정 동안 학업, 실험 및 논문 지도는 물론, 물심양면으로 지원을 해 주신 지도교수님이신 조성학 교수님께 깊은 감사의 말씀을 전합니다. 연구, 논문을 작성하는 방법을 가르쳐 주시고 업무를 수행함에 있어서 가감 없이 조언해 주신 장원석 교수님, 연구자의 바른 자세를 느끼게 해 주셨던 최지연 교수님, 바쁘신 와중에도 논문 심사를 해주신 최두선 교수님, 김재구 교수님, 손익부 교수님 그리고 김주한 교수님께도 머리 숙여 깊이 감사 드립니다.

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국문 초록

본 학위 논문은 산업적으로 활용 가능한 레이저 가공 공정의 개발 및 그 공정을 이용한 연구 내용을 기술하였다. 첫째로, 펨토초 펄스와 대상 재료간의 반응 메커니즘에 기초한 펨토초 레이저 마이크로 가공 공정의 이론적 배경에 대해 소개를 하였다. 두 번째로, 펨토초 레이저를 실제 가공공정에 적용한 두 가지 공정 개발 연구내용으로, 진동자를 이용한 펨토초 레이저 홀 드릴링 가공 기술 개발, Silver nanowire(AgNW)/Carbon nanotube(CNT) 하이브리드 필름 레이저 패터닝 기술의 총 두 가지 응용분야에 대한 연구결과를 수록하였다.

첫째, 진동자 모듈 응용 펨토초 레이저 마이크로 홀 가공에 대한 연구를 수행하였다. 30 ㎛ 두께의 Invar 합금을 대상으로, 진동자 모듈상 진폭과 레이저의 펄스 에너지의 조절을 포함한 파라메터의 변화에 의해 조절되는 테이퍼 각도 조정 공정에 대한 연구를 수행하였다. 실험에는 795nm 파장, 90fs 펄스폭의 펨토초 레이저에 진동자 모듈이 결합된 하이브리드 레이저 시스템으로 명명된 레이저시스템이 사용되었다. 레이저 빔의 초점 위치는 상, 하 방향으로 진동자에 의해 이동이 이루어 진다. 상하 진동 변위는 진동자의 진폭값에 따라서 변화되며, 본 연구에서는 0 ~ 16 ㎛ 범위의 초점 위치의 변화를 사용하였으며, 진동자에 의한 초점위치 변화를 제외한 다른 모든 가공 파라메터는 동일한 조건으로 실험을 진행하였다. 진동의 유무에 따른 가공 형상에 대한 내용을 기술하였으며 가능한 메커니즘에 대한

의견을 기술하였다. 여러 테이퍼 각도의 마이크로 홀 가공 결과를 관찰하였으며, 결과로부터 진동 폭 대비 테이퍼 각도의 차를 가지는 홀 가공 결과를 얻을 수 있었다.

두번째로, silver nanowire (AgNW) / carbon nanotube (CNT) 하이브리드 전도성 필름의 펨토초 레이저 마이크로 가공 연구를 수행하였다. 실험에는 1027nm의 파장, 380fs 의 펄스폭을 가지는 펨토초 레이저가 사용되었다. 어블레이션 실험은 플루언스 값 9.7 mJ/cm^2 부터 70.8 mJ/cm^2 사이의 수치를 적용하여 진행되었으며 어블레이션 문턱값은 13.6mJ/cm^2인 것을 결과로부터 확인하였다. 플루언스 값 65.2mJ/cm^2 까지는 플루언스 값이 오를수록 어블레이션 직경이 급격하게 증가하는 것을 확인하였으며, 플루언스값이 67.9mJ/cm^2 넘은 수치에서는 기판인 유리에 손상이 발생하는 것을 확인하였다. 선 가공을 위한 플루언스 값을 기판에 손상이 가지 않는 최대 수치인 67.9mJ/cm^2 로 정하고 실험이 진행되었다. 선 가공 측정결과에서 완벽하게 가공이 일어난 부분 주변부에 부분적으로 가공이 일어나는 영역이 쉽게 관찰되었다. 레이저 빔이 조사된 부분에 잔여물이 없는 선 가공을 위해서 가우시안 빔 프로파일 대신 준 플랫탑 빔 프로파일을 사용하여 선 가공을 수행하였다. 측정결과 준 플랫탑 빔 프로파일을 사용한 경우 부분적으로 가공되는 부분이 완벽하게 사라지지는 않았지만 확연하게 개선이 된 선 가공 결과를 얻을 수 있었다.

ABSTRACT

Femtosecond laser based high-performance micro-hole drilling on metal with vibration assistance and AgNW/CNT hybrid film patterning

In this dissertation, development of laser micromachining process for industrial applications and those experimental results are described. First, based on interaction mechanism between femtosecond pulse and material, theoretical background of femtosecond laser micromachining process is introduced. Second, two different researches using femtosecond laser are described in the paper as title of femtosecond laser micro hole drilling integrated with vibration module, patterning technique for silver nanowire (AgNW) / carbon nanotube (CNT) hybrid conductive film.

First, femtosecond laser micromachining integrated with vibration module for micro hole drilling has been studied. Thickness of 30 ㎛ Invar alloy is drilled to investigate on angle control of hole taper by changing parameters including amplitude of vibration module and laser pulse energy. Wavelength of 795 nm, pulse width of 90 fs femtosecond laser system integrated with vibration module, so called the hybrid laser system, is used for the experiment. Displacement of focusing position is generated by moving the objective lens vertically by vibration module. The displacement value is range from 0 to 16 ㎛ by following the

amplitude parameter, and the test is conducted without changing parameters except displacement of the focused beam. Comparison between shape of the ablated hole with vibration module and without is reported and discussed about possible mechanisms. Various micro machined holes with different taper angle results are observed, and holes with different taper angle are resulted.

Second, femtosecond laser micromachining for patterning silver nanowire (AgNW) / carbon nanotube (CNT) hybrid conductive film have studied. A femtosecond laser which specifications of 1027nm wavelength and 380fs pulse width is used for the experiment. Ablation test for the AgNW/CNT film is performed at laser fluence values ranging from 9.7 mJ/cm^2 to 70.8 mJ/cm^2, and the threshold of the film is found at 13.6 mJ/cm^2. By increasing laser flunce, diameter of crater is sharply increased until fluence reaches at 65.2 mJ/cm^2, and damage to the glass substrate is observed when fluence is over than 67.9 mJ/cm^2. Fluence value for line pattering is determined as fluence value of 67.9 mJ/cm^2 which is not influenced value to glass substrate. From the measurement result of the patterned line, the irregularly ablated area is easily observed near the completely ablated region. To pattern line without residual at the irradiated area, quasi flat-top beam profile is employed instead of the conventional Gaussian's. The measurement result of the patterned line shows dramatically decreased uneven area when the quasi flat-top energy distribution is used.

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1. Introduction.

1.1. Femtosecond laser micromachining

Since laser has been invented in 1960, laser processing is used as an alternative tool in many applications instead of conventional process for welding, cutting, marking etc. Nowadays, micromachining process with ultrafast laser has been received much attention in the field of manufacturing and research due to precision micromachining characteristics of laser process. Since the first approach for micromachining using ultrafast laser process has been adopted for repairing photo mask, many challenges for industrial applications has been attempted. Precision micromachining with femtosecond laser has embarked on a new view for fabrication for machining in nanometer to micrometer scale because it has advantages for precision micromachining on any materials that are based on non-thermal processing, internal modification, minimal heat affected zone, multiphoton absorption characteristics. Although femtosecond laser micro machining is one of promising technology in laser machining process, it still has several issues to apply for industrial manufacturing including laser stability, cooling system, size of laser system, average power, and pulse energy. Regardless of issues, lots of efforts to connect to industrial application have been made.

In the view of micromachining, ablation results using femtosecond laser are reached with great performance because of the advantages which are introduced above originated from femtosecond regime pulse width [1-3]. There are many researches have been studied by the use of different pulse width of laser on the

same material to compare the ablation result such as dielectrics (e.g., Kuper and Stuke, 1989, Du et al., 1994, Pronko et al., 1995, Stuart et al., 1995-1996, Varel et al., 1996, Ashkenasi et al., 1998, Lenzner et al., 1998, Linde and Sojolowaki-Tintek, 2000) and metals (e.g., Preuss et al., 1995, Kruger and Kautek, 1995, Momma et al., 1996, Nolte et al., 1997, Feuerhake et al., 1998, Wellershoff et al., 1999). In summary of the researches, ablation result with pulse width in the range from nanoseconds to microseconds has limitations for precise micromachining due to thermal effect, mostly. However, micromachining using femtosecond laser is able to suppress thermal effect because of such short pulse width, and micro structure can be fabricated with minimized melting area, cracks, and burr near the structure, consequently. [4-8]

1.2. Overview of interactions between femtosecond pulse and materials

1.2.1. Absorption

Absorption of femtosecond laser should be considered in two ways, linear and non-linear absorption. Normally, status of molecule energy level of is described with the valence band and the conduction band. Also there is a word for the gap between those bands called bandgap. When the photon energy exceeds the bandgap energy, the electrons in the valence band is instantly shifted to the conduction band [9]. In case of metal, the conduction band is partially occupied, which is provided unoccupied energy levels at only slightly higher energy than

occupied one. In this case, photons can be absorbed through free-carrier absorption and gains momentum through an interaction with a phonon (lattice vibration) to move to higher-lying level in the conduction band [10]. When the sufficient laser energy is irradiated into the surface of a material through linear absorption, ablation of the material can occur. When the target material is transparent onto the laser wavelength, excitation for electron with a single photon of light is not enough to move from the valence band to the conduction band, but it can occur with nonlinear absorption. Conventional absorption occurs with single photon absorption (Fig. 1.1). If single photon doesn't have enough energy to excite electrons, absorption does not occur. But when intensively dense photons are irradiated onto the material which is not enough to excite electrons, absorption can occur. To explain this phenomenon, two nonlinear excitation mechanisms are quoted, photoionization and avalanche ionization [11]. In photoionization, electrons in the valence band are directly prompted to the conduction band by photon energy. There are two different regimes of photoionization, the tunneling ionization and multiphoton ionization regime [12]. In tunneling ionization, the electric field of the laser suppresses the potential that binds a valence electron to its parent atom, allowing the electron to tunnel out and become a free electron. In multiphoton ionization, when the extremely high- dense photons are irradiated on material, electrons at the valence band can be excited by multiple photons which photon has smaller energy than that of bandgap. Another mechanism for nonlinear excitation is avalanche ionization. When an electron which is already in the conduction band absorbs photons until it has energy of amount of energy bandgap, then the collision to another electron occurs. Eventually, two electrons at the conduction band are located [11, 13]. Photo ionization during the leading edge of

the laser pulse provides these seed electrons for avalanche ionization until the rest of the pulse. The electron density grows through avalanche ionization until the plasma frequency of the electrons in the conduction band approaches the frequency of the incident laser beam.

1.2.2. Energy relaxation

The initial interaction occurs between photons and electrons as I discussed above. It also means that the time to deposit the energy within the interaction time is determined by the laser pulse duration. After the absorption process, within several picosecond regimes, the energy which is absorbed is redistributed to the various energy states of the system. The energy is transferred from the electrons to the lattice by terms of energy relaxation. In order to understand the difference in the interaction of ultrashort and long laser pulses with matter, the characteristic time scales involved.

If the pulse width is much longer than the time scale of energy relaxation within the system, the whole system will be in equilibrium during the interaction process. In the system, the energy conservation still exists. The change in energy for the system can be described by equation (1) where U is internal energy in volume V, absorption of laser light within this volume $S \cdot V$, energy diffusion out of the volume, $\vec{J}$ the energy flux.

$$\frac{\partial U}{\partial t} = -\nabla(\vec{J} \cdot V) + S \cdot V \qquad (1)$$

This change in internal energy can be connected to a change in temperature T using the specific heat capacity C_i of the material per unit volume ($\partial U/\partial t = C_i \cdot V \cdot \partial t/\partial t$). The heat source S can be calculated taking the energy loss of the laser radiation ($S = -(1-R) \cdot \partial I/\partial z$) into account ($R$ denotes the surface reflectivity and I the laser intensity). Using Beer's law $I(t,z) = I(t) \cdot \exp(-\alpha z)$, this can be simply derived to

$$S = I(t) \cdot A \cdot \alpha \cdot \exp(-\alpha z) \tag{2}$$

where A = 1- R is the surface absorptivity and α is the material absorption coefficient. In most cases the energy loss will be due to heat diffusion, which can be written as [9]

$$\vec{J} = -k \cdot \nabla T \tag{3}$$

Here, k denotes the thermal conductivity. We can now rewrite eq. (1) as

$$C_i \frac{\partial T}{\partial t} = \nabla(k \cdot \nabla T) + S \tag{4}$$

This is the parabolic heat equation. The temperature dependence of the thermophysical parameters (C_i,k) and of the optical parameters (A, α) makes eq.(4) nonlinear, so that its analytical solution can be obtained only in a few

cases [14]. In general, it has to be solved numerically.

We will restrict ourselves here to only a brief discussion of heat transport, in order to obtain an intuitive feeling for typical temporal and spatial scales involved. Assuming constant thermophysical parameters (C_i,k) one can derive from eq. (4) that the resulting heat wave after laser absorption will propagate for about [14]

$$l_{th} \approx \sqrt{D \cdot t} \tag{5}$$

l_{th} is called the heat diffusion length, and $D=k/C_i$ is the thermal diffusivity. For most metals, the thermal diffusivity is typically in the range of 0.1 ~ 1 cm^2/s [14], which means that the heat wave will travel about 0.1 ~ 1 μm within the pulse duration for a 10 ns pulse. Note that this is much longer than the optical penetration depth α^{-1}, which is on the order of 10 nm for metals. Thus, it is appropriate to speak of the laser as a heat source for surface. Since typical laser spot sizes are much larger than the heat diffusion length, heat diffusion will be mainly a one-dimensional heat flow directed normal to the surface in this case.

For short pulse interaction, it is easy to see from eq. (5) that the heat diffusion length becomes equal or even smaller than the optical penetration depth for pulse durations in the picosecond or femtosecond range. Additionally, there is an even more dramatic change in the interaction for these short pulse durations. Now, the laser pulse duration is shorter than the energy relaxation within the system, i.e. the time it takes for the electrons to transfer their energy to the lattice. As a

consequence, heating with ultrashort laser pulses results in strong non-equilibrium conditions. Thus, electrons and lattice have to be described by their own temperatures separately. Such a description, called the two-temperature model (TTM), has been proposed by Anisimov et al. [15],

$$C_e \frac{\partial T_e}{\partial t} = -\frac{\partial Q(z)}{\partial z} - \gamma (T_e - T_i) + S \,, \tag{6}$$

$$C_i \frac{\partial T_i}{\partial t} = \gamma (T_e - T_i) \tag{7}$$

A similar two-temperature model had already been used 20 years earlier to describe the energy relaxation between the electrons and the lattice in order to explain deviations from Ohm's law at high currents [15].

In eqs. 6 and 7, T_e and T_i, denote the electron and lattice temperatures, z is the direction perpendicular to the target surface, and C_e and C_i are the heat capacities of the electron and lattice subsystems, respectively. The parameter γ characterizes the electron-lattice coupling, i.e. the energy exchange between the two systems [15-17]. Measurements reveals values in the range of $\gamma = 10^{16}$-10^{17} W/m^{3}K. $Q(z) = k_e(T_e)\partial T_e / \partial z$ is the heat flux, and $S = I(t) \cdot A \cdot \alpha \cdot \exp(-\alpha z)$ is the laser heating source term. A and α are the surface absorptivity and the material absorption coefficient, $I(t)$ is the laser intensity, and k_e is the electron thermal conductivity. In the above equations, thermal conductivity in the lattice subsystem (phonon component) is neglected because this heat transport occurs on a longer timescale than will be considered here.

The strong non-equilibrium conditions associated with ultrashort pulse

laser interaction with solid makes a detailed theoretical analysis difficult. In principle, the fast and significantly varying properties, including heat capacity, thermal conductivity, relaxation time, reflectivity, and absorption coefficient have to be taken into account by using quantum treatments [17].

By dividing eq.6 and 7 by the corresponding heat capacities C_e and C_i, it can be easily seen that these equations have two characteristic time scales $\tau_e = C_e/\gamma$ and $\tau_i = C_i/\gamma$, where τ_e is the electron cooling time, and τ_i is the lattice heating time. Due to the differences in the heat capacities, it is always true that $\tau_e << \tau_i$. Typical values are the order of 1 ps for τ_e and 0.01 – 1 ns for τ_i. These time scales define three different regimes of interaction, below the time scale of τ_e, above the time scale of τ_i and between them.

If the laser pulse duration τ_L is much longer than the lattice heating time, thermalization between the electron subsystem and the lattice takes place during the laser pulse. In this case, the electrons and lattice can be characterized by a common temperature $T = T_e = T_i$ and eq. (6-7) reduce to the parabolic heat diffusion equation (eq.4) as mentioned before.

For picosecond laser pulses, the condition $\tau_e < \tau_L < \tau_i$ is fulfilled. For times $t >> \tau_e$, eq. (6) for the electron temperature becomes almost stationary, i.e. the energy loss due to heat transport and energy exchange with the lattice is compensated by the energy deposited due to the laser radiation. Accordingly, eq. (6) can be simplified, because $\partial T_e / \partial t = 0$. For times $t << \tau_i$, it is also possible to simplify the equation for the lattice temperature. Due to the quasistationary character of the electron temperature, the lattice temperature will exponentially approach the electron temperature and can thus be expressed as [1]

$$T_i \approx T_e(1 - exp(-\frac{t}{\tau_i})) \approx \frac{t}{\tau_i} T_e \tag{8}$$

An initial lattice temperature has been neglected. It can be seen from this expression that in the picosecond regime, the lattice temperature remains much lower than the electron temperature during the pulse duration. Equilibrium is obtained only after the pulse is over. However, a detailed analysis of this interaction regime depends on the actual material properties.

For the pulse durations much shorter than the electron cooling time, i.e. femtosecond pulses or pulses of a few picosecond duration, the coupling between the electrons and the lattice can be neglected in a first approximation for times $t << \tau_e$. In this case, the differential eq.(4), except that the electron heat capacity has a specific temperature dependence.

An even simpler solution can be obtained when electronic heat transport is neglected, i.e. when the heat diffusion length $l_{th} = (D\tau_e)^{1/2} << \alpha^{-1}$ is much shorter than the optical penetration depth. The electron cooling time has been used here for calculating the heat diffusion length, since the electrons have this time to transport heat before they give their energy to the lattice.

When the electron temperature remains smaller than the Fermi temperature, the electron heat capacity is given by [1, 9, 18]

$$C_e = C'_e T_e = \frac{\pi^2}{2} \frac{n_e k_B^{\ 2}}{E_F} T_e \tag{9}$$

where n_e is the electron density. Within these approximations, the differential equation for the electron temperature reduced to

$$C_e \frac{\partial T_e^{\,2}}{\partial t} = 2I(t)A\alpha exp(-\alpha z) \tag{10}$$

Assuming a constant intensity $I(t) = I_0$, eq.(10) can be directly integrated, yie$_{ld}$ing

$$T_e(t) = \sqrt{\frac{2I_a\alpha}{C_e'} t\, exp(-\alpha z)} \tag{11}$$

In this equations, we have neglected any initial electron temperature $T_0 = T_e$(t=0), and $I_a = I_0 A$ is the absorbed intensity. At the end of the laser pulse, the electron temperature is given by

$$T_e(\tau_L) = \sqrt{\frac{2F_a\alpha}{C_e'} exp(-\alpha z)} \tag{12}$$

where $F_a = I_a \tau_L$ is the absorbed laser fluence.

The evaluation of the electron and lattice temperatures after the laser pulse is described by eq. (6-7) with S=0. After the laser pulse the electrons are rapidly cooled due to the energy transfer to the lattice. Since this cooling time is very short,

eq.(7) can be approximated by [1]

$$T_i \approx \frac{t}{\tau_i} T_e(\tau_L) \tag{13}$$

The attainable lattice temperature is determined by the average cooling time of the electrons $\tau_e{}^a \approx C_e' T_e(\tau_L)/2\gamma$ [1] and given by

$$T_i \approx T_e{}^2(\tau_L)\frac{C_e'}{2C_i} = \frac{F_a \alpha}{C_i} exp(-\alpha z) \tag{14}$$

This lattice temperature distribution is a direct consequence of Beer's law, since heat conduction has been neglected so far. However, if the heat diffusion length $l_{th} >> \alpha^{-1}$ is much longer than the optical penetration depth, a similar calculation of the resulting lattice temperature is possible. In this case, eq.(14) can still be used, provided that we substitute the reciprocal heat diffusion length l_{th}^{-1} for the optical penetration depth α [19].

$$T_i \approx \frac{F_a}{C_i l_{th}} exp(-z/l_{th}) \tag{15}$$

Heat transport in dielectrics and semiconductors is comparably low, since the electrons are not able to escape due to the charge separation force keeping the material neutral. In general, metals show much stronger heat diffusion, since the hot electrons moving into the target can be replaced by cold electrons from the

adjacent region. However, as will be shown below, even in the case of metals heat diffusion can be significantly reduced when ultrashort pulses are used, due to the strong non-equilibrium interactions between electrons and lattice. When the energy of the electrons remains lower than the Fermi energy, the electron thermal conductivity is given by the electron relaxation time, which is determined by electron-phonon and electron-electron collisions $1/\tau = 1/\tau_{e\text{-}ph} + 1/\tau_{e\text{-}e}$ [20]. When the lattice temperature is larger than the Debye temperature, all oscillation modes of the lattice are excited, and a good approximation for the electron-phonon collision frequency can be given by [9, 21] $1/\tau_{e\text{-}ph} \sim k_B T_i/\hbar$. The electron-electron collision frequency can be estimated by $1/\tau_{e\text{-}e} \sim (k_B T_i)^2/\hbar E_F$. While the electrons and the lattice are in equilibrium, $T_e = T_i$, during the interaction of long laser pulses with the metal, the condition $\tau_{e\text{-}ph} < \tau_{e\text{-}e}$ is fulfilled, resulting in $\tau \approx \tau_{e\text{-}ph}$. However, ultrashort laser pulses produce strong non-equilibrium conditions with electron temperatures much higher than the lattice temperature $T_e << T_i$. It means $\tau_{e\text{-}ph} > \tau_{e\text{-}e}$ and therefore $\tau_{e\text{-}ph} \approx \tau_{e\text{-}e}$ also possible. The electron relaxation time is, now we can imagine, determined by the electron-electron collisions. Thus, heat diffusion might be even less for the interaction with ultrashort laser pulses than described by eq.(5) which is dealt with the equilibrium value for the thermal diffusivity.

1.2.3. Ablation

When the ultrashort pulse is irradiated on the material, material ablation occurs by the energy directly or established plasma on the surface. In ablation by the

energy case, the ionization process on the surface happens which generates free electrons conclusively. Because of the much faster energy deposition, ablation with femtosecond laser pulses is different from long pulse (in nanoseconds) laser ablation. In the long pulse laser ablation, the electrons and the lattice remain in thermal equilibrium. During the laser pulse, heat diffuses out of the irradiated area and the material expands. On the contrary, heating with ultrashort laser pulses is a strongly nonequilibrium process. At first, the laser radiation is absorbed inside a surface layer by bound and free electrons. This is accompanied by the excitation and ionization of the material and heating of free electrons by inverse bremsstrahlung, followed by fast energy relaxation within the electron subsystem. Later, energy transfer from the electrons to the lattice, bond breaking, and material expansion take place. For laser fluences close to the ablation threshold the electron-ion energy transfer occurs on a picosecond time scale. In this section, a theoretical description of femtosecond laser ablation of metal targets on the basis of a two temperature model is presented. In the case of metals, laser energy is absorbed by free electrons due to inverse bremsstrahlung. The absorption is followed by fast energy relaxation within the electronic subsystem, thermal diffusion, and energy transfer to the lattice due to electron-phonon coupling. The spatial and temporal evolution of the electron and lattice temperatures in a thin surface layer with subsequent material expansion is described by the following set of one-dimensional equations.

$$C_e \frac{\partial T_e}{\partial t} = -\frac{\partial T_e}{\partial t} - \gamma(T_e - T_i) + S - P_e \frac{\partial u}{\partial x} \tag{16}$$

$$C_e \frac{\partial T_e}{\partial t} = \gamma(T_e - T_i) - (P_i + P_e)\frac{\partial u}{\partial x} \tag{17)}$$

$$\rho \frac{du}{dt} = -\frac{\partial u}{\partial x}(P_c + P_e + P_i) \tag{18}$$

$$\frac{\partial u}{\partial t} + \frac{\partial \rho u}{\partial x} = 0 \tag{19}$$

where x is the direction perpendicular to the target surface, $d/dt = \partial/\partial t + \partial u/\partial x$, and C_e and C_i are the heat capacities of the electron and lattice subsystems, respectively. The parameter γ characterizes the electron-lattice coupling, ρ and u are the density and velocity of the evaporated material, P_e and P_i are the thermal electron and ion pressures, P_c is the elastic pressure, which is positive for compression and negative for expansion, $Q(x) = -(K_e(T_e)\partial T_e)\partial x$ is the heat flux, and $S = I(t)\cdot A\cdot\alpha\cdot\exp(-\alpha z)$ is the laser heating source term. Here, k_e is the electron thermal conductivity, A and α are the surface absorptivity and the material absorption coefficient, and I(t) is the laser intensity. Equations (16) and (17) are energy conservation equations for the electron and ion subsystems. Equations (18) expresses Newton's law and eq.(19) describes the conservation of mass.

In spite of the obvious simplicity of the above equations, their application for modeling of femtosecond laser ablation is problematic. This is due to a lack of reliable information on several parameters that enter into these hydrodynamic equations. For example, there is insufficient information on the equations of state that could describe the evolution of the electron, ion, and cold pressures.

A simple model for ultrashort-pulse laser ablation can be obtained by neglecting the material expansion completely and declaring that one needs a certain amount of energy to initiate ablation. In this case the last term in eq.(16) and (17) containing $\partial u/\partial x$, can be omitted and the hydrodynamic equations reduce to a

one-dimensional two-temperature diffusion model proposed by Anisimov et al.

$$C_e \frac{dT_e}{dt} = -\frac{\partial Q_e(x)}{\partial x} - \gamma(T_e - T_i) + S \tag{20}$$

$$C_e \frac{dT_i}{dt} = \gamma(T_e - T_i) \tag{21}$$

If the laser pulse duration is much longer than the lattice heating time, which is the order of 0.11 – 1 ns, then thermalization between the electron subsystem and the lattice takes place during the laser pulse. In this case, the electrons and the lattice can be characterized by a common temperature $T=T_e=T_i$ and eq.(20) and (21) reduce to the well-known one-dimensional heat diffusion equation

$$C_i \frac{\partial T}{\partial t} = -\frac{\partial}{\partial x} k_e \frac{\partial T}{\partial x} + I(t) A\alpha \exp(-\alpha x) \tag{22}$$

which describes long-pulse laser heating.

For femtosecond laser pulses, the energy transfer to the lattice during the laser pulse and the heat conduction can be neglected in a first approximation. In this simplified case, the ablation rate and the ablation threshold depend only on the optical penetration depth. However, as will be shown below, the interplay of energy exchange between electrons and lattice and the heat diffusion have important consequences, even for ultrashort-pulse ablation. When the heat capacity, the thermal conductivity, and therefore the electron thermal diffusivity are treated as constant, one can find the following equilibrium temperature distribution for the electrons and the lattice after thermal relation

$$T_i \approx \frac{F_a}{C_i}\left(\frac{1}{l^2 - \delta^2}\right)\left[\exp\left(-\frac{x}{l}\right) - \delta \exp\left(-\frac{x}{\delta}\right)\right] \tag{23}$$

Here the optical penetration depth is obtained by $\delta = 1/\alpha$ and the electron thermal diffusion length is given by $l = \sqrt{D\tau_a}$. The duration of the ablation process, τ_a is determined by the time necessary for the energy transfer from the electrons to the lattice. F_a is the absorbed laser fluence.

Two cases, illustrated in figure 1.2, can be distinguished: the optical penetration depth exceeding the thermal diffusion length, $\delta > l$, and vice versa, $l > \delta$. For these cases the following formulas for the equilibrium temperatures can be obtained from eq.(23).

$$T_i \approx \frac{F_a}{C_i \delta}\exp\left(-\frac{x}{\delta}\right) \qquad (\delta > l) \tag{24}$$

$$T_i \approx \frac{F_a}{C_i l}\exp\left(-\frac{x}{l}\right) \qquad (l > \delta) \tag{25}$$

In this simplified model, significant ablation takes place when the energy of the lattice $C_i T_i$ exceeds a certain threshold value. This threshold value can be estimated in a first approximation as the heat of evaporation $\rho\Omega$, where ρ is the density and Ω is the specific heat of evaporation per unit mass. The condition for significant ablation, $C_i T_i \geq \rho\Omega$, can be written as

$$F_a \geq F_{th}^{\delta}\exp\left(\frac{x}{\delta}\right), \quad F_{th}^{\delta} \approx \rho\Omega\delta \qquad (\delta > l) \tag{26}$$

$$F_a \geq F_{th}^{l}\exp\left(\frac{x}{l}\right), \quad F_{th}^{l} \approx \rho\Omega l \qquad (l > \delta) \tag{27}$$

where F_{th}^{δ} and F_{th}^{l} are the corresponding thresholds for the absorbed laser fluence.

The ablation depths are easily derived from eq.(26) and (27)

$$L \approx \delta\hbar(\frac{F_a}{F_{th}^{\delta}})\,(\delta > l) \tag{28}$$

$$L \approx l\hbar(\frac{F_a}{F_{th}^{l}})\,(l > \delta) \tag{29}$$

This means that two logarithmic scaling laws are obtained from the two temperature model. These two ablation regimes have also been observed experimentally for sub-picosecond pulse ablation of Cu. With respect to eq.(28) and (29), these two logarithmic dependencies can be attributed to the optical penetration depth and electronic heat conduction, respectively. In Fig. 1.3 the ablation depth per pulse is shown as a function of laser fluence for 150 fs laser pulses with wavelength of 780 nm irradiating a Cu target. The two ablation regimes, that mean the two different logarithmic dependencies, are clearly visible. The thermal diffusion length can be smaller than the optical penetration depth for fluencies F smaller than 0.5 J/cm^2 is related to changes in the heat conduction due to the strong nonequilibrium between electrons and lattice. Fig. 1.4 shows a comparison of ablation rates for Cu obtained with different pulse durations between 0.5 and 4.8 ps. The ablation regime dominated by the optical penetration depth is accessible only for sub picosecond pulses. For pulses $\tau_l \geq 1ps$ there is already significant heat diffusion during the laser pulse. Therefore, the energy

cannot be deposited in an area determined by the optical penetration depth. In case of Cu, the ablation rates are only slightly dependent on pulse duration for pulses up to ~ 5ps. When the pulse duration is increased further, the ablation rates decrease because of the increasing energy losses caused by heat diffusion.

1.2.4. Femtosecond pulse and heat affected zone

In contrast to ablation by ns and longer pulses in which thermal processes dominate, ablation by ultrafast laser pulses is by nonthermal processes that enable high precision material processing to be realized. This characteristic is attributed to rapid energy deposition in the material. It takes a few hundred fs to a few ps for the electron distribution to reach thermal equilibrium after ultrafast laser irradiation. On the other hand, the energy transfer time from the electron subsystem to the lattice, which induces thermalization, is of the order of 1-100 ps, depending on the electron-phonon coupling strength of the material. Time scale of this process is much longer than the time for the electrons to reach thermal equilibrium. Thus, an ultrafast laser can efficiently cause electron heating and generate a hot electron gas, which is far from equilibrium with the lattice. Consequently, only a very small fraction of the laser pulse energy is transmitted as heat; this result in nonthermal processing that enables high-precision microprocessing to be realized. Even though ultrafast laser pulses mainly induce nonthermal processes, they may still generate heat. However, ultrafast laser pulses suppress the formation of a heat affected zone due to their extremely short pulse widths of several tens of fs to a few ps. This permits high quality microfabrication, even for metals with high thermal conductivities.

1.2.5. Thin film ablation with femtosecond pulse

Patterning of thin film by ultrashort laser pulses can be regarded as another subclass in the area of surface patterning. Laser micromachining of thin films finds many applications in different sectors e.g., repairing of photomasks for lithography, repairing display panel. In thin-film processing, femtosecond laser pulses are perfect tools to achieve superior results compared with alternative lasers or even other processes due to the specific interaction with matter. Especially the well-defined ablation or modification thresholds in combination with wavelength and single or multiphoton absorption can lead to the selective removal of layers without disturbing the underlying substrate or other layers. Also the femtosecond pulse duration provides some advantages in terms of heat conduction. Thermal effects in the surrounding area can be minimized, which is an important requirement both in the vertical and in the lateral direction.

Most of the films cover a thickness range of a few tens to a few hundreds of nanometers. Thus, for many materials, the thickness is in the same range compared with the optical penetration depth. If the film thickness is smaller than the characteristic penetration length, the electrons rapidly reach the film-substrate interface, where they transfer their energy to the lattice ions. In this case, the damage threshold is significantly lowered. Drawing the fluence damage threshold for the ablation of metallic films on insulating substrates versus the film thickness will result in two regimes. Krueger [22] carried out investigations for the ablation of gold films on glass substrates. For extremely thin films, the ablation threshold scales linearly with the thickness and from a certain characteristic value for the

thickness the threshold stays constant. Basically, a number of electrons can ballistically travel up to characteristic length in depth. For thicknesses above characteristic length the film behaves like a bulk material.

1.3. Organization of dissertation.

The dissertation consists of 4 chapters including this chapter. The main purpose and motivation of this dissertation is development of laser processing on application for industry field. The dissertation is organized as follow;

In chapter 1, the basic theory of the femtosecond laser induced in material, ablation mechanism, and beam forming technique are introduced.

In chapter 2, development of micro-drilling process on invar alloy using femtosecond laser integrated with vibration module is introduced. Wavelength of 795 nm, pulse width of 90 fs femtosecond laser system integrated with vibration module is used for the experiment. Displacement of focusing position is generated by moving the objective lens vertically by vibration module. Comparison between shape of the ablated hole with and without vibration module are reported and discussed about possible mechanisms.

In chapter 3, femtosecond laser micromachining for patterning AgNW/CNT hybrid conductive film is introduced. The obstacle of this experiment is difference of the ablation threshold of the AgNW and CNT. Because of the difference of the ablation threshold for each material, the experiment result show the uneven shape on the patterned edge. In order to fabricate a fine ablation shape, the QFT profile is purchased. Resultantly, the performance of edge quality near the ablated area is improved with significant.

Finally, the conclusion of this dissertation with a summary of the researches is given in chapter 4.

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