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Selective Ablation of Thin Films by Ultrashort Laser Pulses

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- Invited Paper -

Abstract

Laser ablation of bulk solid could obtain superior machining accuracy by utilizing ultrashort pulses due to the smaller laser-induced thermal diffusion length, which minimizes the heat affected zone. In selective laser ablation of thin films, the precise control of the heat affected zone in the vertical direction becomes critical in order to avoid the damage of the substrate. For this application an effective thermal penetration depth can be defined determined by not only the optical penetration depth, but also the lattice thermal diffusion length in short pulse ablation or the hot-electron penetration depth in case of ultrashort laser ablation. The ablation characteristics, such as the threshold fluence and the multi-pulse incubation effect, are strongly dependent on the film thickness when it is in the range of the effective thermal penetration depth.

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Keywords: Thin film ablation; ultrashort laser ablation; thermal penetration depth; incubation effect

Nomenclature

\( d \) film thickness
\( \rho \) mass density
\( c, C_l \) heat capacity of the lattice
\( C_e \) heat capacity of the electrons at room temperature
\( k_e \) heat conductivity of the electrons at room temperature

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1. Introduction

The interaction between laser radiation and solids has been investigated extensively for a large variety of materials, for different pulse duration and spectral domains. Sufficient evidence reveals that the laser induced temperature profile in temporal and spatial distributions plays a significant role in the initial stage of material ablation, although afterwards thermally induced stress, plasma and shockwave will be possibly involved [1-2]. The laser energy deposition into the material starts from the photon-electron interaction and the temperature rise is due to the elevation of the kinetic energy of the lattice through electron-lattice energy exchange [3-4]. Usually the removal process takes place as material melting or evaporation. The ablation geometry is highly dependent on the temperature distribution governed by the laser absorption profile and the heat diffusion length. In many cases, the heat diffusion length was discussed in laser ablation of solids demonstrated from the accuracy in lateral direction. By experimental observation, the heat diffusion length determines the heat affected zone (HAZ) surrounding the ablation spot. The HAZ is found to be strongly dependent on the applied pulse length. A shorter pulse provides smaller heat affected zones and higher ablation accuracies. In the selective laser ablation of thin films, besides the lateral resolution, the precise ablation in vertical direction is also critical. In order to avoid damage of the substrate, the ablation crater has to be restricted to the thin film thickness. In this case, both optical penetration depth and heat diffusion length have to be taken into consideration, because both affect the temperature distribution during the pulse irradiation. The depth to which the heat effect can reach during a laser pulse can be defined as effective thermal penetration depth. In Ref.[5] Dausinger simply treated the effective thermal penetration depth by adding the optical penetration depth and thermal diffusion length. In Ref.[6-7] the authors pointed out that for the effective optical penetration depth both the optical penetration depth and the electron heat penetration depth have to be taken into consideration for ultrashort pulse laser ablation of metals. It is difficult to give an explicit math expression from theoretical derivation. Here we express the effective penetration depth as:

\[ \text{Effective penetration depth} = l_{opt} + l_{th} \]
where the operator ‘‘’’ represents the co-effect of optical penetration and thermal diffusion. For strongly absorbing materials like metals where \( l_{\text{opt}} \ll l_{\text{th}} \) is fulfilled, it is justified to treat the laser source as a surface heat source. Hence the thermal penetration depth is mainly determined by the heat diffusion length. It is well-known in the short pulse regime, e.g. nanosecond pulse ablation that the thermal penetration depth is found to be proportional to the square root of the applied pulse length [8]:

\[
I_{\text{eff}} \approx \sqrt{2 \chi \tau_p} .
\]  

In the ultrashort pulse regime, the situation is more complex because the photon-electron and electron-electron coupling time are on the same order of the pulse length, where hot electron scattering plays a dominate role in the transportation of heat and phonon-phonon coupling could be neglected. In this case the thermal penetration depth is mainly caused by the electrons. In case when surface lattice melting occurs, it can be calculated for metals by using the TTM model [9]:

\[
I_{\text{eff}} \approx \left( \frac{128}{\pi} \right)^{1/8} \left( \frac{k_e^2 C_l}{C_m T_m g^2} \right)^{1/4}.
\]  

However, for wide-bandgap semitransparent materials which exhibit a large optical penetration depth, where \( l_{\text{opt}} \gg l_{\text{th}} \) is valid, the absorption of the laser energy has to be treated as a volume heat source. The effective thermal penetration depends on both the optical penetration and the thermal diffusion. In this case it is difficult to give an explicit math expression from theoretical derivation. In Ref.[10], the authors investigated the thermal confinement volume in the short pulse regime, a volume where the energy gained from the laser irradiation is higher than the thermal conduction losses. They found the penetration depth of such confined volume is proportional to the optical penetration depth and the applied pulse duration. It becomes even more complicated in ultrashort pulse ablation of such material because of the nonlinear laser absorption processes. Both optical penetration depth and heat diffusion length are found to be dependent on the laser intensity.

\[ F_{\text{th}} \]

![Fig. 1. Schematic illustration of the ablation threshold change dependent on the applied pulse duration](image-url)
The relation of the thermal penetration depth and the pulse length can be indirectly described by the change of the damage threshold versus pulse length. For short pulse ablation a $\tau_p^{1/2}$ scaling rule is found for both metals and semiconductors. In the ultrashort pulse regime, the ablation threshold stays almost constant for metals, but a nonlinear feature is observed for semiconductors [11], schematically shown in figure 1. A characteristic time $\tau_c$ can be defined, which distinguishes the different dependence of the ablation threshold fluence on the pulse length, as expressed in the following equation for metals [9]:

$$\tau_c \approx \left( \frac{8}{\pi} \right)^{1/4} \left( \frac{C_t^3}{C_c^2 T_m g^2} \right)^{1/2}.$$ (4)

In bulk material ablation, the laser generated heat is free to conduct from the surface into the volume. The characteristic time $\tau_c$ separates the short and ultrashort pulses regimes in the field of laser ablation. However, when a film-substrate system is investigated, the absorption depth and the heat diffusion length are often limited by the film thickness, which could involve the influence from the substrate and affect the thermal distribution for a specific pulse length.

2. Investigation on Ablation Behavior Dependent on Film Thickness

2.1. Threshold fluence by single-pulse ablation

The influence of the metal film thickness on the ablation characteristics has been studied for different pulse duration regimes [12-15]. Figure 2(a) shows the dependence of the ablation threshold fluence on the thickness of tungsten films which were deposited on silicon substrates. For picoseconds laser ablation, the obtained threshold data can be divided into two regimes. For films below a thickness of 95 nm, the thresholds increase with thickness. For thicker films, $d > 95$ nm, the ablation threshold keeps constant and remains the bulk ablation threshold value. The effective thermal penetration length can be determined to 95 nm, which separates the film and bulk ablation features for tungsten. In most studies which deal with metal films, the influence of film thickness on the damage threshold exhibits two distinguished regimes. However, by taking very thin film into investigation, a third regime can be observed. As shown in Ref.[16] by femtosecond laser ablation of very thin gold films, if the film thickness is in the range of optical penetration depth, the ablation threshold fluence is found to decrease with film thickness. In summary, the threshold as a function of film thickness can divide into three regimes for metals. It starts decrease with the film thickness. When it exceeds the optical penetration depth it becomes increase as the rising of the thickness and finally exhibits as a constant like ablation of bulk material if the film thickness reaching the effective thermal penetration depth. Consequently it is reasonable to express ablation threshold dependence on the film thickness as the plotted solid curve shown in figure 2(a). Although the laser pulse parameters such as the pulse length or laser wavelength will affect the ablation threshold value, it always reveals these three distinguished regimes for metal films when the condition $l_{opt} << l_{th}$ is fulfilled.
Based on the behavior of highly absorbing materials, we investigated the ablation of transparent ITO films on glass substrates with different thicknesses. Figure 2(b) illustrates the ablation threshold over film thickness for femtosecond and picosecond pulse ablation. The dependence of the ablation threshold fluence \( F_{th} \) on the film thickness \( d \) for ITO films demonstrates two regimes, in contrast to metals where three regimes can be identified. For very thin films, the ablation threshold fluence decreases as the film thickness increases, similar to the case of metals when its thickness is in the range of optical penetration depth. The decreasing trend changes when the film thickness exceeds a certain value. Here the effective thermal penetration depth is defined. It stays at a constant value similar to the case of bulk material ablation. It should be noted that the optical penetration depth of ITO is \(~ 2 \mu m\) at 1064 nm for linear absorption part (\( \alpha \approx 5.3 \times 10^5 \text{ cm}^{-1} \)). The thermal diffusion length is \(~ 15 \text{ nm}\) calculated by \( \sqrt{\frac{2 \tau}{\pi}} \) for 10 ps pulse length. It differs from metals by \( l_{opt} \gg l_{th} \) for the low absorption of ITO films.

2.2. Incubation effect in multi-pulse ablation

Laser induced damage to a material surface under multi-pulse irradiation demonstrates an interesting phenomenon: the material surface becomes damaged at pulse energies far below the single-shot ablation threshold, so called incubation effect. In most investigations of laser ablation of thick metals, it was reported that the multi-pulse ablation threshold fluence satisfies [17]:

\[
F_{th}(N) = F_{th}(1) N^{S-1}. \tag{5}
\]

In case of multi-pulse ablation of bulk dielectric or some semiconductor materials, a different incubation model was proposed [18]:

\[
F_{th}(N) = F_{th}(\infty) + [F_{th}(1) - F_{th}(\infty)]e^{-S(N-1)}. \tag{6}
\]
Fig. 3. In a logarithmic plot the ablation thresholds decrease over the number of pulses. (a) For gold films, the lines are fitted to Eq. 6. (b) For ITO films, the lines are fitted to Eq. 5. with only the filled data points are used for the fitting. Both graphs are obtained by 10 ps pulses at 1064 nm wavelength.

However, through the experiment, the incubation phenomenon of multi-pulse ablation of film reveals a different behavior, when the film thickness is in the range of thermal penetration depth. The experiment results of the threshold fluence dependent on the number of applied pulses are shown in figure 3. In contrast to bulk materials the incubation can be distinguished for metal films by Eq. 6 whereas the best approximation for ITO is attained for Eq. 5. The largest differences between single- and multi-pulse of laser induced damage occur for the thickest films, which gets higher cumulative influence, shown in figure 3(a). In contrast, for wide-bandgap ITO films a strong cumulative effect occurs for with irradiation few pulses on thinner films. The thresholds drop with the increasing number of incident pulses. However, beyond a specific number of pulses the fluence threshold stays constant. The threshold value turned to its final value with less pulses for thick films. The relationship between threshold and pulse number is able to be quantitatively described by Eq. 5, as shown in figure 3(b) by the dotted lines fitted with excluding the points which reached the final threshold value for high pulse numbers. It is interesting to note that a similar incubation coefficient $S=0.82$ can be calculated for all films [19].

3. Theoretical Analysis of Thermal Penetration Depth

In order to describe the dependence of the threshold fluence on film thickness, we assume a pure photothermal effect is responsible for the observed ablation effects. The onset of ablation is defined when the temperature reaches the melting point and finally a molten phase can be observed. Neglecting the lateral heat diffusion and only considering the depth due to the large beam size compared to the film thickness, the temperature rise in the heated volume due to the absorption of laser energy can be expressed by:

$$\Delta T_m = \Delta Q / C_l. \quad (7)$$

A simplified model for the threshold fluence can be obtained based on Eq. 7 written in the form [13]:

$$F_{th} = \frac{\Delta T_m}{(1-e^{-\alpha d})(1-R)}\left[\rho_f c_f - \left(\frac{l_{th,s}}{l_{th,f}}\right)\rho_s c_s\right] L_f + \frac{\Delta T_m}{(1-e^{-\alpha d})(1-R)} l_{th,f} \rho_s c_s, \quad (8)$$

where the subscripts $f$ and $s$ denote the film and substrate quantities, respectively. $L_f$ is the minimum
dimension of the heated volume, which can be the film thickness, the optical penetration depth or the effective thermal penetration length. From this equation the different regimes of the threshold behavior for metal and ITO films can be derived.

For metal films $l_{\text{opt}} < l_{\text{th}}$ and $l_{\text{eff}} \sim l_{\text{th}}$, the ablation threshold dependence on film thickness can be characterized by three regimes:

- In the first regime, $d < l_{\text{opt}} < l_{\text{eff}}$ and $L_f = d$ are fulfilled. For small $d$ the limit of the first term in the Eq. 8 is found:

$$\lim_{d \to 0} \frac{d}{1 - e^{-\alpha d}} = \frac{1}{\alpha}$$

(9)

However, for the second term which represents the influence of the substrate, the limit converges to the infinity because $(1 - e^{-\alpha d}) \sim 0$ when $d \to 0$. This implies that as film becomes thinner, the substrate influence increases and more pulse energy is required to promote the film to reach its melting temperature. $F_{\text{th}} \sim d^{-1}$ is found.

- In the second regime, $l_{\text{opt}} < d < l_{\text{eff}}$ and $L_f = d$ are fulfilled. In this case the pulse energy is regarded to be totally absorbed, where the term $(1 - e^{-\alpha d}) \sim 1$. Also the influence from the substrate is limited. Easily one can find that $F_{\text{th}} \sim d$ is established.

- In the third regime, $l_{\text{opt}} < l_{\text{eff}} < d$ and $L_f = l_{\text{eff}}$ are fulfilled. The laser energy is regarded to be totally absorbed and the heated volume is limited by $l_{\text{eff}}$. The influence from the substrate can be neglected. Hence the ablation threshold $F_{\text{th}}$ is no longer dependent on the film thickness and behaves similar to the ablation of bulk material.

For transparent ITO films $l_{\text{opt}} >> l_{\text{th}}$, the ablation threshold dependence on film thickness can be characterized in two regimes:

- In the first regime, $d < l_{\text{eff}} < l_{\text{opt}}$ and $L_f = d$ are fulfilled. Similar to the case of metal films in first regime, the substrate influence plays a dominate role for the ablation threshold fluence. $F_{\text{th}}$ decreases with increasing film thickness.

- In the second regime, $l_{\text{eff}} < d < l_{\text{opt}}$ and $L_f = l_{\text{eff}}$ are fulfilled. Because of the large optical penetration depth $l_{\text{opt}}$, a variation of the film thickness $d$ in this regime only leads to a very small change of the $(1 - e^{-\alpha d})$ term, which can be regarded approximately as constant. On the other hand, the heated volume is controlled by $l_{\text{eff}}$ which is independent of the film thickness $d$. Therefore, $F_{\text{th}}$ stays approximately constant.

In multi-pulse laser ablation of bulk solid material, the incubation effect for metals is attributed to the surface stress-strain energy storage. The multi-pulse irradiation on a site is similar to the mechanical fatigue damage. In the analogy to the fatigue failure induced by the stress for $N$ cycles one could obtain Eq. 5 [17]. For the dielectric bulk materials or some semiconductor materials, the incubation effect can be attributed to laser induced defects. Due to the bandgap, multi-shot irradiation onto a site could induce the generation of point defects by multi-photon excitation, for example formation of color centers [20-21]. The strength of such accumulation process is related to the excitation and generation of electrons initiated by combined multi-photon absorption and avalanche ionization. The threshold fades due to the decrease of defect accumulation for increasing $N$ until reaching a constant level. Based on this assumption Eq. 6 is proposed to depict the incubation effect. In case of multi-pulse ablation of metal films thinner than the effective thermal penetration depth, the strengthen of the surface modification is regarded to be responsible for the enhanced incubation effect, rather than storage of strain-stress energy for the bulk metal samples [22]. In contrast, the residual of the mechanical stress-strain energy is regarded to be the reason for multi-pulse ablation of ITO film when its thickness becomes smaller than the effective thermal penetration depth.
It has to be mentioned that the effective thermal penetration depth $l_{\text{eff}}$ is the co-effect of the optical penetration and the thermal diffusion (the thermal carrier maybe the lattices or the electrons). From the experiments of threshold fluence dependent on the film thickness, the effective thermal penetration depth $l_{\text{eff}}$ can be easily determined, which separates the film and bulk features in laser ablation.

4. Conclusion

In this paper the effective thermal penetration depth for both metals and transparent ITO films are discussed. For metals, the thermal penetration depth can be analytically calculated by treating the laser as surface heat source. Due to the complicated nonlinear absorption of laser pulses for transparent semiconductors, a theoretical prediction of thermal penetration depth is difficult. By experimentally measuring the relation of the ablation threshold fluence dependent on the film thickness, the effective thermal penetration depth for both metal and ITO films can be obtained. When the film thickness is in the range of thermal penetration depth, the influence from the substrate can not be neglected and the ablation features such as the threshold fluence and the incubation effect in multi-pulse ablation are heavily dependent on the film thickness. This is very different to the ablation of bulk material.

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