Picosecond Laser Ablation of Indium Tin Oxide Thin Film

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For my parents, my daughter Shuxin and my wife Li Zhou.
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Abstract

Picosecond Laser Ablation of Indium Tin Oxide Thin Film

Thin film based on applications is of interest in many industries. Laser selective patterning of thin films often is used to generate certain functionalities. A considerable challenge that still remains in laser patterning is the understanding of the thermal penetration depth which affects the laser selective ablation of film and substrate system. Through the laser ablation of films with different thicknesses, the thermal penetration depth can be obtained for both high absorption metal and low absorption semiconductor indium tin oxide (ITO) films. We demonstrate that the optical penetration depth and the thermal diffusion length play a significant role in determining the thermal penetration depth. The film thickness affects the ablation threshold for metal and ITO films if the thickness is in the range of thermal penetration depth. Laser ablation of ITO films on glass through the front- and rear-side are investigated to demonstrate the influence of the thermal penetration depth.

We have performed experimental studies on the incubation effect existed in the multi-pulse ablation for different film thickness. We found that for the films in the thickness of thermal penetration depth, the incubation behavior fits a different theoretical model compared to ablation of bulk material by multi-pulses. As pulse laser structuring of lines or areas are the result of applying of multi-overlapped pulses, the influence of the incubation effect on the laser ablation of ITO films will be discussed.

The influence of substrate on laser selective patterning of ITO film will be discussed. Ablation of ITO films by thermal evaporation or stress-assisted delamination will be discussed for PET-based substrates. The parametric optimizing of picosecond laser selective ablation of ITO film on PET substrate will be demonstrated.
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Chapter 1

Introduction

1.1 Laser Ablation

Laser originated as an acronym for light amplification by stimulated emission of radiation, a device that emits light through a process of optical amplification based on the stimulated emission of photons from the gain medium by the supply of pump energy [7]. It took many years since the publication of the basic theoretical principle of the stimulated emission of radiation by Einstein in 1917, until the first laser was demonstrated by T.H. Maiman in 1960 [8]. The basic principle of the laser configuration is shown in figure 1.1(a). The essential elements of a laser include a gain medium, pumping process achieving a population inversion and optical feedback element. Since the first invention, the lasers have experienced an incremental and steady development, different types of lasers were invented with various gain media (gas, liquid or solid) operating in either continuous or pulsed mode with a wavelength from ultraviolet to far-infrared [9]. Today lasers are almost everywhere, from laser-pointers and supermarket checkouts, to space exploration and telecommunication.

Laser ablation is a process of removing material from a target surface by coupling the laser energy into the target material [10,11]. A schematic illustration of laser ablation is shown in figure 1.1(b). Normally, a strong or even violent photon-matter interaction at high photon flux can be observed. In the first two
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decades after the laser invention, the laser was principally used in emission and mass spectrometry for chemical analysis. It is not only after 1980’s, when the first practical laser ablation application was realized by producing high critical temperature superconductor films, the potential of laser ablation started to be exhibited [12]. Due to the intrinsic properties of lasers, several advantages in laser processing of material are exhibited over the traditional methods, such as non-contact, no solvent chemicals, selective material removal and flexibility. The development of pulsed laser sources enhanced the laser application in material mass removal for their attainable high laser intensities, especially the emergence of the short and ultra-short pulsed lasers, which are of benefit to contemporary pulse compression technologies. Such laser sources become promising tools for machining with sub-micrometer or even nanometer precision. The shorter pulse duration in laser ablation reduces the heat diffusion related to fast laser–matter interaction, leading to higher precision, improved resolution and better surface and volume localization. The precise controllability of pulse duration, output energy and wavelength attracts a great deal of attention for laser ablation in both fundamental research and technological applications. For instance laser structuring, laser direct deposition, laser-based medical surgery and so on. Figure 1.2 illustrates some typical examples of laser ablation.

Selective laser patterning refers to ablation of a thin film in multi-layered
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Figure 1.2: Examples of laser ablation applications. (a). Laser in-situ keratomileusis. (Source: Stephen Siebert, Laser Focus, Adelaide, Australia) (b). Laser micro drilling. (Source: Laser Automation GeKratronic SA, Switzerland) (c). Laser micromachining of Hyotube stent. (Source: Larry Dosser, MLPC Inc., Miamisburg, USA)

materials with no damage or minimum damage to the other layers. It mainly takes the advantage of the monochrome property of the laser. Usually each layer material has a distinct spectral absorption behavior, as well as a difference of the thermal response to the laser excitation. This gives a chance to confine of laser-matter interaction in the desired layer. Nowadays thin films are extensively used in various fields of applications. Thin film drives the application in modern electronics like flat panel displays, photovoltaic, micro batteries and so on. An attractive potential of thin-film-based devices is the possibility to make these electronics light in weight and flexible in carry. However, in practical applications precise structuring and sophisticated alignment of each layer is required. For example, the multi-touch panel made for smart phones consists of at least ten layers of material and thousands of structured pixels enabling the capacitive signals for the gesturing features. In thin film solar cells, in order to improve the out-put performance, the film has to be structured to form several single cells with serial interconnection, as schematically shown in figure 1.3.

As the structures required in device production become more complex, the selective machining of these functional thin films is a challenge. Initially the majority of the patterning tasks are performed using some type of photolithography,
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Figure 1.3: The multilayered structure of thin-film based organic solar cells. Each layer is required to be selectively patterned for serial interconnection to improve the output performance.

A traditional technique involving multiple steps, including photo-resist coating, baking, exposure, developing, material etching and photo-resist stripping. This is a complex process requiring large capital investment in equipment, high fabrication costs, high maintenance charges, and long fabrication times. Versatile technologies are required for patterning thin-film materials on rigid and flexible substrates. The large-area applications of thin films, such as photovoltaic, require high speed and simple-to-use techniques. Laser processing with its flexibility is one of the most promising methods to achieve high quality material etching. When the laser beam is focused onto the multi-layered material target, the laser-matter interaction is highly dependent on the absorption of the material at a specific laser wavelength, the peak power density and the pulse duration of the laser. Using optimized laser parameters, it is possible to localize the ablation in the expected layer.
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1.2 State of Research in Laser Ablation of ITO Film

For most of the applications the ITO layer has to be structured with special patterns. Wet etching, plasma etching and laser direct-writing are the main adopted methods in industry. Wet etching gives a high process yield but requires high equipment investment and complicated steps like resist coating, optical lithography, developing, etching and resist stripping [13, 14]. For large area devices like solar cells, it tends to produce different ITO etch rates depending on the deposition methods in addition to isotropic etching and selective grain-boundary etching, which makes it quite difficult to obtain uniform patterns for hard control of etching depth, so called under- and over-etching [15]. As an alternative, plasma etching offers high resolution, but it requires corrosive gases like Ar/CH$_4$ and also photolithography [16]. Laser direct-writing for its high process speed, maskless and environmentally friendly properties, obtained intensive research interest.

The earliest research into laser patterning of ITO thin films used a KrF excimer laser operating at 248 nm with ns pulse length. The authors showed the possibility of laser selective removal of ITO film on glass and pointed out that the thermal vaporization was the reason for the film loss [17, 18]. Yavas and co-workers conducted the processing of ITO thin films using a pulsed DPSS laser with various wavelengths of 1047 nm, 532 nm, 349 nm and 262 nm at 15 ns pulse duration [19–21]. Shoulders were observed around the perimeter of the etched areas, approximately 100 nm higher than the original surface of the layer in their experiments. The formation of these shoulders was regarded as an attribute to the surface tension gradients of the melted liquid plume under the incident of Gaussian beam. Apparently thermal evaporation was identified for the film removal for all wavelengths. Ashkensai et. al. performed trials with different pulse lengths from 150 fs to 5 ps on glass samples coated with 150 nm thick ITO films at a wavelength of 800 nm [22]. The results showed that the films could
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be cleanly removed using a multi-pulse processing strategy, and confirmed that the ablation mechanism is a thermal process for the applied pulses. Račiukaitus et. al. published the results of ITO patterning trials using picosecond lasers at visible and ultra-violet wavelengths of 532 nm, 355 nm and 266 nm [23]. Similar patterning processes using picosecond lasers were reported by Risch [24]. Harrison et. al. [25] and Chen et. al. [26] analyzed the ITO thin film patterning with spatial laser beam shaping from Gaussian to Top-hat to decrease the shoulder-like lines. Most investigations so far indicate that photo-thermal evaporation is the main reason for the film removal.

However, some exceptions were reported by Szörenyi et. al., who conducted the ablation of ITO films on glass substrates with a 248 nm excimer laser [27]. They found that thin films were more likely to be removed by mechanical delamination in a cleaner manner, as observed for the 70 nm and 160 nm films studied. The thicker films were regarded to be removed by thermal evaporation, for example with 400 nm and 500 nm films in their experiments. The thermo-elastic force was found to play a role in detaching the ITO film from the glass substrate by a spatially modulated pulsed Nd-YAG laser beam with wavelength of 1064 nm and pulse width of 6 ns [28].

1.3 Objective and Organization of the Thesis

The main content of this thesis focuses on the investigation of picosecond laser ablation of ITO semiconductor films. Aimed at advancing the knowledge of picosecond laser selective patterning of ITO films for industrial applications, we performed experimental and theoretical analysis on the ablation process by different configurations, for example comparison of the influence of pulse width, film thicknesses and substrates, etc.

The thesis is organized as follows:

• Chapter 2 presents the fundamental theory of pulsed laser interaction with
solids. Starting from the excitation of electrons, laser ablation of materials undergo several complicated interaction processes. The difference in threshold fluence as function of pulse length for metals and semiconductors will be discussed. On the other hand, laser induced mechanical stress generation will be demonstrated, which could also result in material loss under some conditions.

- Chapter 3 introduces the laser ablation setup, the optical and thermal properties of the materials and some basic ablation features by Gaussian laser beam.

- Chapter 4 discusses the thermal penetration depth in laser ablation. Concerning the laser ablation of thin films, a thermal penetration depth can be defined which separates the bulk and thin film regimes distinguished by different ablation characteristics, for example the ablation threshold fluences. For metals it can be obtained by both theoretical prediction or experimental means. However, for semiconductors like ITO material, it is difficult to provide a theoretical prediction due to both consideration of thermal diffusion length and optical penetration depth. However, through the investigation of the laser ablation threshold fluences dependent on the ITO film thickness, it can be determined experimentally. The influence of the thermal penetration depth on the ablation process is illustrated by an example, where the different ablation characteristics are observed by front- and rear-side irradiation for samples with different film thicknesses.

- Chapter 5 studies the incubation effect and its influence on laser patterning of ITO film. In multi-pulse ablation, the material will cumulate the damage effect exhibited by the reduction of the ablation threshold. The variation trends of the ablation threshold fluences dependent on pulse number reveals the different cumulative mechanisms for metal and ITO films. Furthermore, how the incubation effect changes regarding the film thickness will be investigated.
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- In Chapter 6 the influence of substrate on laser selective patterning of ITO film will be discussed. Several mechanisms exist in laser patterning of ITO film on different substrates, such as thermal evaporation or stress-assisted delamination. The picosecond laser ablation of ITO film on PET substrate is found to be based on a different processing mechanism from the film on glass substrate. With parametric optimization, the possibility of picosecond laser selective ablation of ITO film on PET substrate will be demonstrated.

- The conclusion of the present work and recommendations for future research are provided in Chapter 7.
Chapter 2

Fundamental Physical Processes of Laser-Matter Interaction

In this chapter, the fundamental physical processes of pulsed laser interaction with metals and semiconductors will be presented. Behind the extensive applications of laser ablation, the underlying microscopic collective physical processes of laser-matter interaction are regarded as being quite complex, strongly depending on the parameters of the laser pulse and the properties of the target material. The material removal could be the result of laser induced thermal evaporation or stress-assisted spallation.

2.1 Laser-Matter Excitation

When laser irradiation is performed on a target surface, the interaction of laser and material will cause reflection, absorption and transmission of the incident light, shown in figure 2.1. The electromagnetic radiation of laser passes over the electrons and exerts a force and sets the electrons into motion by impacting from electric field. The absorbed radiation near surface region of the bulk material down to a penetration depth is defined by the laser frequency (wavelength) and the material electronic band structure. The absorption strength of laser irradia-
2. Fundamental Physical Processes of Laser-Matter Interaction

Figure 2.1: Schematic demonstration of the absorption, reflection and transmission of laser beam when irradiating onto a target.

Absorption in the material is generally expressed in terms of the Beer-Lambert’s law [8]:

\[ I(z) = I_0(1 - R)e^{-\delta z} \] \hspace{1cm} (2.1)

where \( I(z) \) is the laser intensity (W/cm\(^2\)) at depth, \( R \) is the surface reflectivity and \( \delta \) is the material’s absorption coefficient (cm\(^{-1}\)). Normally \( \delta \) is the function of the laser wavelength. According to equation 2.1 the intensity of the laser radiation gets attenuated inside the material. The length over which the significant attenuation of the laser radiation takes place is often referred to as optical penetration depth given by the reciprocal of the absorption coefficient [29]:

\[ l_{opt} = \delta^{-1} \] \hspace{1cm} (2.2)

As mentioned before, the laser radiation is essentially an electromagnetic wave, the energy deposition is through the interaction of the electromagnetic waves with the free or bound electrons of the target. Therefore, the laser-matter excitation is heavily dependent on the electronic band structure of the material. For a metal, the Fermi level is inside the conduction band. There is no bandgap since the va-
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lence band overlaps the conduction band and a significant fraction of the valence electrons can move through the material [30], which are called free electrons. In this case, the optical absorption is usually dominated by free-carrier absorption, which excites electrons in the conduction band to a higher-lying level by Inverse Bremsstrahlung and gains energy from laser beam, shown in figure 2.2(a) [31]. It is known as its high absorption and reflection in a wide spectrum range. For example, in the visible and infrared spectral region, the linear absorption coefficient \( \delta \) of metals is in the range \((5 -10) \times 10^5 \text{ cm}^{-1}\), resulting in an optical absorption depth \( l_{\text{opt}} \) in the order of \(10 \sim 20 \text{ nm} \) [9]. For semiconductors, photons can be absorbed through free-carrier absorption in the conduction band at low laser intensity. More often, due to lack of an appreciable population of free electrons as metallic materials, electrons in the valence band are expected to contribute to the optical response by high intensity laser irradiation. The bandgap energy, \( E_g \), between the conduction and valence bands defines the amount of energy needed to excite an electron from the highest level of the valence band to the lowest level of the conduction band [1]. If a single-photon energy is larger than the semiconductor bandgap \( h\nu > E_g \), single-photon absorption could happen which excites a valence electron to the conduction band, referred to as interband absorption, as shown in figure 2.2(b). If the bandgap energy is greater than the photon energy \( h\nu < E_g \), there are two classes of excitation mechanisms that play a role in the laser absorption: photoionization and avalanche ionization [32]. The photoionization includes two different regimes depending on the laser frequency and intensity, the tunneling ionization regime and the multi-photon ionization regime [33]. 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. This type of ionization dominates for strong laser fields and low laser frequency. At higher laser frequencies, but still below that required for a single-photon absorption, the multi-photon absorption with simultaneous absorption of multiple photons by an electron can occur, as shown in figure 2.2(c). The sum of the energy of all the photons absorbed must exceed...
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the bandgap energy, $n\hbar \nu > E_g$. Multi-photon absorption requires $n$ photons to interact simultaneously with a single electron, so the probability for absorption will scale as the density of the photons raises to the power $n$. Because photon density is proportional to laser intensity $I$, the probability for multi-photon absorption scales as $I^n$. Avalanche ionization involves free-carrier absorption by an electron already in the conduction band of the material followed by impact ionization. An electron in the conduction band sequentially absorbs several laser photons until its energy exceeds the conduction band minimum by more than the bandgap energy, then collisionally ionizes another electron, leaving two electrons at the conduction band minimum $[32,34]$, as illustrated in figure 2.2(d). As long as the laser field is present, this process repeats and the electron density in the conduction band grows exponentially $[35]$.

It is a linear absorption process if the laser energy is deposited into a material through free-carrier absorption and interband single-photon absorption. The absorption strength is independent on the laser intensity in this case. If the photoionization or avalanche ionization occurs a nonlinear absorption process is identified, where the absorption probability is a nonlinear function of the laser intensity.

The laser-matter interaction generates a highly non-equilibrium state of excited free carriers. The free carriers are redistributed throughout carrier-carrier and carrier-phonon scattering. When an equilibrium electron energy and a Fermi-Dirac distribution are established, the diffusion of hot electrons is driven by the temperature gradient $[36]$. In the carrier-phonon scattering process, the charged free carriers release their energy by spontaneous phonon emission, which transfers energy to the lattice and increases the temperature of the lattice. Carrier-carrier and carrier-phonon collisions occur concurrently during the first few hundred femtoseconds after excitation. It takes several picoseconds before the carriers and the lattice to reach thermal equilibrium. When the free carriers and the lattice come to an equilibrium temperature, the temperature of laser-excited material can be defined by conventional heat conduction means. The typical time scales of the
interaction chain of events can be crudely classified as shown in figure 2.3 [1, 2].

After the thermalization the spatial distribution of the energy can be characterized by the temperature profile. It is justified to describe the further evolution in terms of thermal processes. The generation of heat and its conduction into the material establish the temperature gradient, which is highly dependent on the applied pulse parameters and the thermo-physical properties of the material. If the incident laser intensity is sufficiently high, the absorption of laser energy can result in the phase transformations of the target, such as melting and evaporation. Figure 2.4 schematically presents the typical thermal effects induced by laser-matter interaction [9]. Generally, the phase transformations are associated with threshold (minimum) laser intensities, referred to as melting and evaporation.

Figure 2.2: Laser excitation of electrons. The linear absorption including (a). free-carrier absorption, (b). interband single-photon absorption. The nonlinear optical process is found in (c). interband multi-photon absorption, (d). avalanche ionization.
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thresholds ($I_m$ and $I_v$). Melting and evaporation are efficient material removal mechanisms in many laser machining applications.

Furthermore, the ionization of vapor during high laser intensity irradiation may lead to generation of plasma due to the growing of electron density. At this stage the high density plasma plume strongly absorbs the laser energy by free-carrier absorption and attenuates the laser energy reaching the target. The plasma plume expansion could also lead to the generation of stress wave [37]. On the other hand, the laser-matter interactions are associated with mechanical stress due to the thermal expansion or the propagation of shockwave, which could cause another kind of ablation form exhibits as spallation in case the amplitude exceeds the bounding strength of lattice in the target.

2.2 Thermal Diffusion in Laser Ablation

The above mentioned carrier excitation and energy exchange can be subdivided in several ultrafast processes which have been crudely classified by the timescale

![Different time scale in the laser excitation of materials](image)

Figure 2.3: Different time scale in the laser excitation of materials [1, 2].
as shown in figure 2.3. The carrier excitation happens at a time of several femtosecond order. The carrier-carrier and carrier-phonon energy coupling occurs in a time of sub-picosecond level. And heating of the lattice happens at approximately 50 ∼ 200 ps. Usually after a few tens of picosecond the relaxation of energy exchange between electrons and lattice will complete. The time to deposit the energy within these states is determined by the laser pulse duration.

It is instructive to define a characteristic time $\tau_c$ to depict the time required for the construction of thermal equilibrium between electron and lattice subsystems, as shown in figure 2.3. The general so-called short and ultra-short pulses can be separated by the characteristic time $\tau_c$.

## 2.2.1 Short pulse ablation

In the regime where the pulse width is longer than the characteristic time $\tau_p > \tau_c$ (but still in nanosecond scale), although the laser radiation energy is transferred
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to the electrons initially, the electrons coupling their energy to the lattice on a
timescale shorter than the pulse width. Thus, the electrons and the lattice remain
in thermal equilibrium and the thermal wave propagation is mainly due to the
heat conduction by lattice. Typically the optical penetration depth $l_{opt}$ is much
smaller than lateral dimension, which is in the scale of laser spot size. By treating
laser as a conventional heat source, the energy transport in the material can be
described by the Fourier heat conduction model in this case [38], written in one
dimension as:

$$\rho C \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} k \frac{\partial T}{\partial z} + S(z, t). \tag{2.3}$$

Here $\rho$ denotes the mass density, $C$ is the heat capacity and $k$ is the thermal
conductivity. The laser source item $S(z, t)$ obeys the Beer-Lambert absorption
law by:

$$S(z, t) = \frac{dI(z, t)}{dz} = \delta(1 - R)I(t) \exp(-\delta z). \tag{2.4}$$

The equations can be solved easily by numerical methods. Figure 2.5 shows
an example of the evolution of the surface temperature for ITO irradiated with
nanosecond pulse solved by numerical calculation. The exact analytical solution
of equation 2.3-2.4 is complicated. However, an approximate solution can be
reached for high absorption materials. When $l_{opt} \ll \sqrt{\chi \tau_p}$ is fulfilled, where
$\chi = k/\rho C$ is the thermal diffusivity, the short pulse laser energy is absorbed in a
very thin layer which can be treated as a surface heat source like most metals. In
this case the equation can be solved by regarding the laser irradiation as a Dirac
flux in both spatial and temporal fields [38], given as:

$$T_\delta(z, t) = \frac{F_a}{\rho C \sqrt{\chi \pi t}} \cdot \exp\left(-\frac{z^2}{4 \chi t}\right). \tag{2.5}$$

Here $F_a = (1 - R)I_0 \tau_p$ is the absorbed laser fluence. Equation 2.5 describes the
temperature decay after the pulse irradiation, providing a quite well approaching
description for most metals. Similar to that of the single frequency modulated
waves and optical penetration depth, we can define a thermal diffusion length, $l_{th}$, at which the temperature decayed to be $1/e$ of the surface value [39]:

$$l_{th} = \sqrt{2\chi \tau_p}.$$  \hspace{1cm} (2.6)

Figure 2.5: Time decay of the maximum surface temperature induced by 10 ns pulse irradiation on ITO surface. The thermal properties of the material used in the simulation can be found in Table 3.2. The laser pulse is plotted in a dashed line in arbitrary unit.

If the target material has a low absorption to the laser pulse, for example if $l_{opt}$ is comparable to $\sqrt{\chi \tau_p}$, the analytical solution is found to be complicated.

### 2.2.2 Ultra-short pulse ablation

For pulse duration shorter than the characteristic time $\tau_p < \tau_c$, the Fourier heat conduction model is no longer valid. In this case the temperature for electron and the lattice subsystems have to be considered separately. For metals, the energy
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Figure 2.6: Time decay of the maximum electron and lattice temperature in irradiation onto gold surface by a 100 fs pulse obtained from TTM calculation.

exchange between the electrons and the lattice subsystems can be expressed by the so-called two-temperature model (TTM), proposed by Anisimov et al. [40]. The TTM describes the temporal and spatial evolution of the lattice and electron temperatures, $T_l$ and $T_e$, in the irradiated target by two coupled nonlinear differential equations:

$$
\begin{align*}
C_e \frac{\partial T_e}{\partial t} &= \frac{\partial}{\partial z} k_e \frac{\partial T_e}{\partial z} - g(T_e - T_l) + S(z,t), \\
C_l \frac{\partial T_l}{\partial t} &= g(T_e - T_l).
\end{align*}
$$

(2.7)

where $C_l, C_e$ are the heat capacities and $k_l, k_e$ are the thermal conductivities of the electrons and the lattice as denoted by subscripts $e$ and $l$. The heat diffusion is mainly contributed by the electron subsystem. The heat diffusion of the lattice is neglected because it only happens at the longer timescale. $g$ is the electron-phonon coupling factor related to the rate of energy exchange between the electrons and the lattice. $S(z,t)$ is a source term describing the local energy deposition by the laser pulse shown in equation 2.4.
Figure 2.6 shows an example of the numerical simulation results for femtosecond laser induced the temperature rising for gold surface as function of time. Due to the small heat capacity of electrons, \( C_e \ll C_l \), we see the temperature of the electrons increases very quickly in the first few femtoseconds and reaches extremely high peak temperature. After several tens of picoseconds, depending on the electron-lattice coupling coefficient \( g \), the electron and the lattice temperature reach thermal equilibrium. If the incident laser energy is sufficiently high, the lattice can reach its melting temperature, or even the evaporation point, before the electron and lattice obtain thermal equilibrium. In case the pulse duration \( \tau_p \) is smaller than some relaxation time \( \tau_R \), part of the electron energy transferring to the lattice can be neglected during the pulse duration for analytical solutions. Therefore, the electron-lattice coupling term is neglected in the TTM equation.

It has been noted that \( C_e \) and \( k_e \) are time dependent variables, where \( C_e = C_0 T_e \), \( k_e = k_0 (T_e / T_l) \) and \( C_0 \), \( k_0 \) are temperature independent constants. The first equation describing the electron temperature in 2.7 can be rearranged as:

\[
C_0 \frac{\partial T_e^2}{\partial t} = k_0 \frac{T_l}{T_l} \cdot \frac{\partial^2 T_e^2}{\partial z^2} + 2S. \tag{2.8}
\]

It can be solved using Dirac flux approaching found as

\[
T_e^2 = \frac{2F_a}{C_0} \sqrt{\frac{C_0 T_l}{\pi k_0 t}} \exp\left(-\frac{C_0 T_l}{4k_0 t} z^2\right), \tag{2.9}
\]

\( F_a \) is the absorbed laser fluence. From this equation the time-dependent electron diffusion length for \( T_e^2 \), similar to the thermal diffusion length in short-pulse cases, is obtained:

\[
X_e = \sqrt{\frac{2k_0}{C_0 T_l} t}. \tag{2.10}
\]

Subsequently the surface electron temperature as a function of \( X_e \) becomes:

\[
T_e = \left(\frac{8}{\pi}\right)^{1/4} \left(\frac{F_a}{X_e C_0}\right)^{1/2}. \tag{2.11}
\]
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The electron energy relaxation time $\tau_R$, which can be estimated by keeping only the second term on the right-hand side of the first equation in 2.7 and neglecting $T_l$ in that term, given by:

$$\tau_R = C_0 T_e / g.$$  \hspace{1cm} (2.12)

In case the lattice reaches the material melting temperature $T_m$ after the relaxation time $\tau_e$, $T_l = T_e = T_m$ is fulfilled. If the absorbed threshold fluence $F_a$ necessary for the heat confined volume satisfies the equation:

$$F_a = C_l \Delta T_l X_e \simeq C_l T_m X_e.$$  \hspace{1cm} (2.13)

From equation 2.11-2.13, one can obtain the characteristic heat diffusion length in ultra-short laser ablation of metals as [41]:

$$l_R = X_e (\tau_R) \simeq \left( \frac{128}{\pi} \right)^{1/8} \left( \frac{k_0^2 C_l}{C_0 T_m g^2} \right)^{1/4}.$$  \hspace{1cm} (2.14)

The equation 2.14 shows the distance the electrons penetrate before the energy coupling to the lattice is dependent on the electron-lattice coupling coefficient $g$. Usually it is several hundred nanometers thick in metals, exceeded by a large factor, the value of the thermal diffusion length $l_{th}$ that would be predicted by the classic heat conduction equation or the $l_{opt}$ in the very short pulse case. For examples, for gold sample irradiated by femtosecond laser, $l_{th}$ is usually $\sim20$ nm and $l_{opt}$ is $\sim10$ nm, but $l_R$ can reach to $\sim100$ nm.

For the ultra-short pulse ablation, another feature can be found for the dependence of ablation depth on the applied pulse fluence. For long pulse ablation, due to the long lifetime of melted liquid plume, the dependence of the ablation depth on the applied fluence can only be analyzed statistically. However, for ultra-short pulse an identified logarithm dependence of ablation depth per pulse on the laser fluence can be found. For the scenario of metal ablation described by TTM model in equation 2.7, solving the approximate expression for attainable
lattice temperature one can obtain \[3\]:

\[
T_l \simeq \frac{F_a}{C_l l_{th}^2 - l_{opt}^2} \left[ l_{th} \exp(-\frac{z}{l_{th}}) - l_{opt} \exp(-\frac{z}{l_{opt}}) \right].
\] (2.15)

From the equation, using the conditions for significant evaporation \(C_l T_l \geq \rho \Omega\), here \(\Omega\) is the specific heat per unit mass of evaporation. Two regimes can be distinguished:

- In the low fluence regime, the density of hot electrons is considered to be low enough that the energy transfer between the electrons and the lattice occurs only within the area characterized by the optical penetration depth \(l_{opt}\) [42–44]. In this case the ablation depth per pulse is written as:

\[
L \approx l_{opt} \ln(F_a/F_{th}) \quad (l_{opt} > l_{th}, \quad F_{th} \simeq l_{opt} \rho \Omega)
\] (2.16)

- In the high fluence regime, with generation of high density of hot electrons and strong electron-phonon energy coupling, the ablation rate increases dependents on the lattice thermal diffusion velocity as:

\[
L \approx l_{th} \ln(F_a/F_{th}) \quad (l_{opt} < l_{th}, \quad F_{th} \simeq l_{th} \rho \Omega)
\] (2.17)

The two dependence regimes of the ablation rate versus the pulse fluence were experimentally confirmed for metals by ultra-short pulse ablation, as shown in figure 2.7.

For ultra-short pulse ablation of semiconductors, the situation is more complex than metals due to the conductive electron density changes by the optical excitation. With the consideration of phonon excitation and relaxation separated into the optical and acoustic modes for the lattice response, it is possible to characterize the energy transportation by the balance for free-carrier density, free-carrier energy and lattice energy. The energy balance equations for elec-
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Figure 2.7: Typical dependence of the ablation rate on the incident laser fluence for ultra-short pulse ablation, high and low pulse fluence regimes can be determined [3].

electrons and lattice subsystems have been constructed by Choi and Grigoropoulos in the case of a silicon target irradiated by 800 nm, 100 fs laser pulses [45]. By solving sets of coupled equations, spatial and temporal evolutions of the electron and lattice temperatures for the first few ps of material evolution were obtained. Based on similar equations, S. Mao calculated the laser fluence threshold for silicon melting where they found the calculated values were in good agreement with the experimental data for 35 ps, 532 nm laser pulses incident normally onto the silicon surface [46].

2.2.3 Threshold fluence dependent on pulse width

From the above analysis, the thermal equilibrium time $\tau_c$ is significant important in determining the short and ultra-short pulse ablation, which shows different heat diffusion mechanisms during the laser-matter interaction. In case the pulse width is in nanosecond regime, the lattice will dominate the heat diffusion process. As described in equation 2.5, the laser induced heat diffusion length is confined by $l_{th}$. Regarding the condition of significant evaporation and ablation, $C_lT_l \geq \rho \Omega$, one can find the relation between the threshold fluence and the pulse width, written
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as

\[ F_{th} \simeq l_{th} \rho \Omega. \]  

(2.18)

Noted that \( l_{th} \sim \sqrt{\chi \tau_p} \), one can find that, for short pulse ablation, the threshold fluence is dependent on the square root law of the pulse width, well-known as \( F_{th} \propto \tau_p^{1/2} \). However, for ultra-short pulse ablation, due to the fast diffusion of the highly energetic electrons which makes the lattice thermal diffusion effect safety neglected, the required laser fluence to initial the evaporation of the heated volume is governed by the effective laser energy deposition depth \( l_{eff} \) rather than \( l_{th} \), expressed as

\[ F_{th} \simeq l_{eff} \rho \Omega. \]  

(2.19)

For metals, in the ultra-short pulse regime the effective laser energy deposition depth \( l_{eff} \) is determined by the hot electron energy transport, as shown in equation 2.14, \( l_{eff} \sim l_R \), which is independent on the pulse duration. Therefore, the ablation threshold is almost constant over the pulse duration change in ultra short pulse regime. For semiconductors, the hot carrier density changes over the pulse intensity, as well as the energy loss being a more complex form like photo emission, avalanche recombination etc. As a consequence, the ablation threshold fluence for these materials exhibits as a nonlinear function of the pulse duration in ultra-short pulse regime.

There exists a characteristic time variable \( \tau_c \), from which the short and ultra-short pulse can be separated and different heat diffusion features can be observed. By equation 2.12 and equation 2.10, \( \tau_c \) can be obtained analytically for metals [41]:

\[ \tau_c = \left( \frac{8}{\pi} \right)^{1/4} \left( \frac{C_i^3}{C_0 T_{m} g z} \right)^{1/2}. \]  

(2.20)

The characteristic time \( \tau_c \) can be experimentally obtained for both metals and semiconductors through the threshold change over the logarithm of pulse duration, \( F_{th} \ln(\tau_p) \). Usually the characteristic time \( \tau_c \) is found in the range of several tens of picoseconds for different materials. Figure 2.8 shows the ablation thresh-
old fluence dependent on the pulse duration for both metals and semiconductors obtained from experiments [4]. It is worth seeing the threshold fluence dependent on pulse duration shifts from the square root law to almost independent on the pulse duration for metals and nonlinear relationships for semiconductors. As

![Graph](image1.png)

(a). Au film.

![Graph](image2.png)

(b). Fused silica film.

Figure 2.8: Pulse-length dependence of damage threshold of (a). a gold film and (b). fused silica by laser pulse at 1053 nm [4].

mentioned, the laser energy deposition depth is dependent on the characteristic time $\tau_c$, which is found to play a significant role in thin film ablation as discussed later.
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2.3 Mechanical Stress in Laser Ablation

During the laser-matter interaction, there has been experimental evidence that absorption of laser pulse energy not only induces thermal effect in target, but also creates mechanical stress. Under certain conditions, it could play an important role in laser ablation. One observation is that the energy density for ablation can be up to several orders of magnitude lower than that needed for complete evaporation [47]. The material removal with low threshold points strongly to laser induced mechanical stress effects being implicated. Another observation is that ablation with short pulses is always accompanied by the radiation of strong acoustic waves, which can lead to thermo-elastic stress [5] in the material. The rapid release of this stresses causes the emission of acoustic waves. Certain fraction of the absorbed laser energy goes into elastic strain-stress energy and a fraction thereof into plastic deformation of the target, generation of cracks or voids and converting to the kinetic energy of the ejected fragments. In contrast to the thermal induced evaporation loss, the transient stress-induced material damage and loss is known from shockwave research as “spallation” in solid ablation, schematically show in figure 2.9 [5].

The atomic-level molecular dynamics (MD) simulation reveals the existence of the internal stress for metals [48,49], organic solid [50] and a solid argon [51]. The comparison between experiment and atomistic simulations provides an insight into thermo-mechanical dynamics of ultra-short pulse irradiation on metal films [52–54]. By extending molecular dynamics simulation to the experimental micrometer length scale, Demaske et. al. observed the complete dynamics of gold films subjected to ultra-short laser irradiation and found the ablation of the melt at the front, and crack nucleation then spallation at the rear side of the sample. For thick films (> 0.5μm in their case) ablation and spallation are spatially separated; whereas for thin films they merge into a unique damage process [54]. Figure 2.10 shows how an example, stress wave is generated by high-intensity and ultra-short pulse laser heating on gold thin film, where the stress wave propaga-
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tion starts from the surface into the material as the function of time is observed. Figure 2.11 illustrates the snapshots of atoms behavior when irradiated by the laser pulse. The thermal evaporation occurs at the film surface and meanwhile the void forms inside the solid induced by internal stress which is observed.

From the discussion in reference [5], the photomechanical ablation happens if both thermal confinement and inertial stress confinement are fulfilled. The thermal confinement conditions occur when the pulse duration is shorter than the characteristic thermal relaxation time $t_{th}$, given by

$$ t_{th} = \frac{d^2}{4\chi}, $$

(2.21)

where $d$ is the smallest dimension of the heated volume determined by the optical

Figure 2.9: (a). Thermal expansion of the volume heated by a laser pulse causes mechanical stresses; (b). Upon propagation from the free surface, a tensile component develops with gradually increasing amplitude; (c). At some depth the tensile strength is exceeded and the material fractures; (d) (e). Detachment and ejection of material from the front surface. The figures are referred to [5].

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Figure 2.10: MD simulation of 120 fs laser pulse irradiates on gold surface with fluence 0.12 J/cm². The laser irradiates the front surface located at z = 60 nm and the back surface is constrained at z = 0. The front surface moves due to the thermal expansion and the stress wave propagation can be observed in the depth of material.
penetration depth or the beam size, whichever is smaller. The inertial stress confinement is achieved if the heating pulse is much shorter than the characteristic time of acoustic relaxation $t_{ac}$ given by

$$t_{ac} = \frac{d}{c_s},$$

(2.22)

where $c_s$ is the speed of sound. In case of layered medium, if there is an acoustical mismatch from high to low acoustic impedance ($Z = \rho c_s$), the stress wave is partly (or fully at a free boundary) reflected and will accumulate lots of energy at the layer interface. The acoustic resistance is defined by

$$R_z = \frac{Z_1 - Z_2}{Z_1 + Z_2},$$

(2.23)

where $Z_1$ and $Z_2$ are the acoustic impedances of the target and the surrounding medium. On the other hand, the misfit of the thermal expansion for different
2. Fundamental Physical Processes of Laser-Matter Interaction

layers will cause additional stress.
Chapter 3

Experimental Setup and Material Properties

3.1 Laser Ablation System

The laser mainly used in this study is a HYPER RAPID 25 laser (Lumera Lasers GmbH). The laser is a passively mode-locked solid state Nd:YVO4 laser and generates pulses with a duration of a few picoseconds with a repetition rate of 50 MHz. The pulse repetition rate is reduced with a pulse picker based on an electro-optical modulator (EOM). The output repetition rate is between 200 kHz and 1000 kHz. The fundamental wavelength of the laser is 1064 nm (infrared light). With second- and third harmonic generation (SHG and THG) 532 nm (green light) and 355 nm (ultraviolet light) laser light can be generated. Because the laser emits a TEM$_{00}$ mode the beam can be described as a Gaussian beam. Some key parameters of the laser are listed in Table 3.1 below. Pulse chain is assessed by controlling the open time of external electro-optic modulator (EOM), which is capable of repetition rates up to 200 kHz.

The laser output power can be adjusted in discrete steps. Figure 3.1 shows the laser output power for the three wavelengths for different power adjustment steps at a frequency of 200 kHz. The power for the 1064 nm wavelength is higher than the two others because of the lower efficiency of the harmonic generation.
3. Experimental Setup and Material Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>1064 nm, 532 nm, 355 nm</td>
</tr>
<tr>
<td>Pulse repetition rate</td>
<td>200 - 1000 kHz</td>
</tr>
<tr>
<td>Spatial mode</td>
<td>TEM(_{00}) ((M^2 &lt; 1.3))</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>10 ps</td>
</tr>
<tr>
<td>Beam divergence, full angle</td>
<td>&lt; 1 mrad</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>≈ 3 mm at 1064 nm</td>
</tr>
</tbody>
</table>

Table 3.1: Parameters of HYPER RAPID 25 picosecond laser.

Figure 3.1: Relation of the laser output power and the adjustable motor step.
the beams leave the laser they are expanded by a 3x Galilean beam expander (BE03M, ThorLabs). Then the beam is guided with mirrors into a scanner. The beams with 1064 nm and 532 nm wavelengths are guided into a hurrySCAN II 14 scanner, the 355 nm light is guided into a hurrySCAN II 10 scanner (ScanLab GmbH). The function of the scanners is to move the beam in x-y direction relative to the sample surface and to focus the beam. Therefore they are equipped with F-theta lenses (LINOS). The sample is positioned onto a motion stage (Physic Instrument GmbH).

The laser ablation system is schematically shown in figure 3.2. With the stage the sample can be moved in xyz-direction. The laser, the scanner and the stage are controlled with special software running on a computer. The software controls the scanning speed and motion, the power of the laser, the laser frequency and the motion of the stage. Beside coordinate based data input the software is able to handle various file types like the DXF and STL format, which are widely used for computer-aided manufacturing, or pictures in BMP file format for complex structures.

The femtosecond laser (Spitfire, Spectra-Physics Inc.) used in the experiment
emits 150 $fs$ pulses at wavelength of 800 $nm$ with a repetition rate of $1 \ kHz$. The beam diameter exhibits 7 $mm$ with a quality parameter of $M^2 = 1.3$. A galvo-scanner with a F-theta lens (LINOS) is equipped.

Another microsecond laser (SLS 200 CL16, LASAG Inc.) used in the experiments emits 300 $ms$ pulses at 1064 $nm$ wavelength. This system utilizes an optical fiber to delivery the beam and equips a focusing kits (LLBK 45) to guide the beam to the sample. Motion stages (Physic Instrument, GmbH) are integrated to move the samples for structuring.

3.2 Material Properties

The term of transparent conducting oxide (TCO) refers to the heavily doped oxide semiconductors. They have a bandgap sufficiently large ($\geq 3 \ eV$) to make them optically transparent over the visible spectral range and own a high concentration of free carrier to give them high electrical conductivity. Indium tin oxide (ITO) is an n-type semiconductor of such TCO materials with a large bandgap ($3.5 - 4.3 \ eV$) and a high concentration of free carriers ($> 10^{20} \ cm^{-3}$), possing the advantages of high electrical conductivity and high transmittance in the visible part of the spectrum. For undoped $\text{In}_2\text{O}_3$ which has a direct bandgap of about 3.75 $eV$, the Fermi energy $E_F$ is located in the middle of the bandgap and the conduction band is empty [55]. With the introduce of low density of Sn donor atoms, subsequently, the conduction band is partly filled and its Fermi level $E_F$ comes close to the conduction band. With the optimization of the Sn doping concentration, about 10 wt%, about $1.5 \times 10^{21} \ /cm^3$ of free carrier density can be obtained [56]. Such high free carrier density makes ITO film exhibit the metallic properties, such as low resistivity, high reflectivity in infrared regime and so on.

Figure 3.3 gives an overview of the fundamental physical properties and the mechanisms governing the optical performance of ITO [6]. Through the measurements made by UV-VIS spectrophotometry, the optical transmission spectra for
Figure 3.3: Fundamental physical processes and mechanisms for transparent and conducting ITO films. $E_g$ is fundamental semiconductor bandgap, $\hbar \omega_p$ is plasmon energy, and $\hbar \omega_{ph}$ is phonon energy [6].

Figure 3.4: Effect of the film thickness on the optical transmission for ITO films deposited on the glass substrates.
3. Experimental Setup and Material Properties

different thicknesses of ITO films are shown in figure 3.4. The films composed of 90 wt% In$_2$O$_3$ and 10 wt% SnO with different thicknesses, were deposited on the soda lime glass substrates. The film thickness was determined by spectroscopic ellipsometry. The optical properties of ITO in the spectral range of interest from 300 \textit{nm} to 1200 \textit{nm} are controlled by different types of electronic excitation, where three different regions can be distinguished. In the ultraviolet (UV) region, a UV photon can excite an electron from the valence band directly to the conduction band (interband absorption). The excitations across the fundamental bandgap $E_g$ gives a strong absorption in this regime [57]. In the visible region, the transmittance is very high. The variation in the transmission are increased as the film increases due to interference phenomena. In the near infrared (NIR) it is almost opaque because of free carrier absorption, an infrared photon can excite an electron from near the bottom of the conduction band to higher within the conduction band. The material exhibits high reflectivity with metallic properties due to the free electron excitation in this regime.

![Figure 3.5: Transmittance of ITO films on Glass and on PET samples. The films are 100 \textit{nm} thick.](image)
3. Experimental Setup and Material Properties

<table>
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<tr>
<th>Property</th>
<th>Unit</th>
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<th>Glass</th>
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<td>GPa</td>
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<tr>
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</tr>
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<td>[18,25,58,59]</td>
<td>[60,61]</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Table 3.2: Typical thermal and optical properties of ITO, PET and glass.

The ITO films with thickness of 100 nm coated on PET (Polyethylene terephthalate) substrates (ITOPET 50, VisionTek Ltd) were also used in the experiment. Figure 3.5 shows the measured transmittance of the same thickness of ITO film on glass and PET substrate. It is obviously that the glass samples shows a better optical transparency. The thermal and optical properties are important to understand the different behavior of the ITO films on the two substrates. Table 3.2 shows some key properties of the used materials. The samples are exposed to laser irradiation as purchased without any further treatment.

3.3 Results Analysis Methods

Various analysis methods are used for the characterization of the ablation results. A simple way to characterize the sample damage is the usage of optical microscopy. For analyzing the processed samples, a binocular microscope (MBL 2000, Krüss) is used. Beside various zooming factors, a digital camera (Canon EOS 450D) is mounted to take photographic pictures. The main disadvantage is, that this method provides only few vertical information about the etching depth and the profile.

A white-light interferometer (TMS-1200, TopMap $\mu$.Lab, Polytech GmbH) is used to measure the dimensions of the irradiated area. It provides information
3. Experimental Setup and Material Properties

about the depth, width and height with nanometer precision. Figure 3.6 shows the schematic layout of the white-light interferometer. The depth and width of the ablated spots and lines can be measured also by a stylus profilometer (XP-2, Ambios Technology). The stylus profilometer uses a diamond tipped stylus to scan across the sample surface and measures the surface topography of thin and thick films. The vertical movements of the stylus is measured and recorded simultaneously during the scanning, which reveals the topographical structure of the surface. The instrument has vertical resolution in nanometers and horizontal resolution as small as twenty nanometers and measures the film thicknesses from 5 nm and over 500 µm.

To get more accurate information about the shape of the spots a scanning electron microscope (SEM) is used. The advantages of a SEM are its huge magnification, its large depth of field and the high resolution (4-10 nm). The SEM

Figure 3.6: The schematic layout of the white-light interferometer.
3. Experimental Setup and Material Properties

machine is equipped with add-on analytical Energy-dispersive X-ray spectroscopy (EDX) used for the elemental analysis to show locally ITO film removal on the substrates.

3.4 Ablation with Gaussian Beam

Most of lasers are operated on the fundamental transverse mode ($TEM_{00}$), where the emission beam intensity distributions are well approximated by Gaussian functions. The spatial and temporal profile of a pulsed laser intensity can be expressed as:

$$ I(r, t) = I_0 e^{x(-\frac{2r^2}{\omega_0^2})}e^{x(-\frac{2t^2}{\tau_p^2})} \quad (3.1) $$

where $I_0$ (W/cm$^2$) is the peak intensity at the center, $\omega_0$ is the spatial radius (beam waist) and $\tau_p$ is temporal radius (pulse duration) at the 1/e$^2$ intensity contours, $r$ is the radius coordinate of the distance from the propagation axis and $t$ is the time. The peak intensity can be obtained by

$$ I_0 = \frac{2}{\pi \omega_0^2} \cdot \frac{P_{\text{avg}}}{\tau_p f}. \quad (3.2) $$

Here $P_{\text{avg}}$ (W) is the average power and $f$ (Hz) is the pulse repetition rate. Therefore, the spatial distribution of the pulse fluence can be determined by

$$ F(r) = \int_{-\infty}^{+\infty} I(r, t)dt = F_0 e^{\frac{-2r^2(\omega_0^2)}{\tau_p^2}}, \quad (3.3) $$

where $F_0 = I_0 \tau_p \sqrt{\pi} / 2$ (J/cm$^2$) is the peak fluence. The peak pulse fluence and the peak energy $E_p$ (J) are related by

$$ E_p = \int_0^{\infty} F(r)2\pi rdr = \int_0^{\infty} F_0 e^{\frac{-2r^2(\omega_0^2)}{\tau_p^2}}2\pi rdr = \frac{\pi \omega_0^2}{2} F_0. \quad (3.4) $$
3. Experimental Setup and Material Properties

From this equation we can obtain the calculation of pulse fluence as:

\[ F_0 = \frac{2E_p}{\pi \omega_0^2}. \]  \hspace{1cm} (3.5)

Usually the ablation exhibits a deterministic threshold fluence \( F_{th} \), where the maximum laser fluence can be applied without initiation of the ablation of the material. Based on the Gaussian description of the incident laser beam, the ablation spots diameter \( D \) and the applied peak laser fluence \( F \) above the threshold fluence can be related based on equation 3.3 by:

\[ D^2 = 2\omega_0^2 \ln\left(\frac{F}{F_{th}}\right). \]  \hspace{1cm} (3.6)

From this equation, by plotting squared-diameters of the ablated spots produced with different pulse energies in a logarithmic scale with a linear fitting manipulation, the threshold fluence \( F_{th} \) can be obtained by extrapolating the linear curve resulting from this fitting to zero diameter and the effective beam size \( \omega_0 \) can be calculated from the slope [62]. In case of multi-pulse ablation, the ablation threshold \( F_{th}(N) \) can be determined with the same process corresponding to the relation of \( D^2(N) \) and \( F \).

The film ablation is subjected to be positioned at the focus plane, where the maximum ablation efficiency can be obtained, because for a Gaussian beam propagating along \( z \) axis, the minimum beam size \( \omega_0 \) can be found at the focus plane. The variation of the beam size along the \( z \) axis is defined by

\[ \omega(z) = \omega_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}, \]  \hspace{1cm} (3.7)

where \( z_R = \pi \omega_0^2 / \lambda \) is the Rayleigh length. Based on equation 3.7 the focus position can be determined by \( z \) scan. For example, figure 3.7 shows the experimental results for picosecond laser ablation system. Here the beam waist about 20 \( \mu m \) at the focus position is calculated for 1064 nm. Through a similar way we can
3. Experimental Setup and Material Properties

Figure 3.7: Gaussian beam size at different z position obtained from experiments. Find the focus positions and beam sizes for femtosecond and microsecond lasers.
Chapter 4
Effective Thermal Penetration Depth of ITO Film

In this chapter laser-induced effective thermal penetration depth will be investigated. In laser processing of thin film, the challenge is not only from the ablation accuracy in lateral dimension, but also in a vertical direction where minimizing the thermal damage to the substrate is required. When the film thickness is in the range of effective thermal penetration depth, the laser ablation characteristics demonstrate different behavior compared to the ablation of bulk material, for instance, which can be exhibited through the ablation threshold fluence variation dependent on the film thickness. The effective thermal penetration depth influences on the laser ablation of ITO film through front- and rear-side irradiations will also be studied.

4.1 Introduction

The interaction between laser radiation with solids has been investigated extensively for a large variety of materials, in different time and spectral domains. Sufficient evidence reveals that laser induced temperature profiles in temporal and spatial distributions play a significant role in the initial stage of material ablation, although afterwards thermally induced stress, plasma and shockwave
Effective Thermal Penetration Depth of ITO Film

will possibly be involved [63,64]. The laser energy deposition to the material starts from the photon-electron interaction and the temperature rising is due to the elevation of the kinetic energy of the lattice through electron-lattice energy exchange [36,65]. Usually the removal process is represented as material melting or evaporation. The ablation spots 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 \( l_{th} \) was discussed in laser ablation of solids. It was directly reflected from the ablation accuracy in a lateral direction. As observed in the experiments, \( l_{th} \) determines the size of heat affected zone around the ablation spots. For shorter pulse ablation, the smaller \( l_{th} \) provides a smaller heat affected zone and results in a higher ablation accuracy. Concerning the laser selective ablation of film, besides the ablation accuracy in the lateral axis, the precise ablation in vertical direction is also critical, where the localization or concentration of the laser pulse energy in the film is normally required. In this case, both optical penetration depth and heat diffusion length has to be considered which affects the temperature distribution simultaneously during the pulse irradiation. The depth to which the heat is affected by a laser pulse can be defined as effective thermal penetration depth. In reference [66], Dausinger treated the effective thermal penetration depth by simply adding the optical penetration depth and thermal diffusion length together. In reference [42,44] the authors defines an effective optical penetration depth, which takes the hot electron penetration depth into consideration when talking about the optical penetration in ultra-short laser ablation of metals. Here we defined the effective penetration depth as:

\[
 l_{eff} = l_{opt} \oplus l_{th}. \tag{4.1}
\]

The operation \( \oplus \) stands for the results are the co-effect from the both sides.

For strong optical absorption materials like metals where \( l_{th} \gg l_{opt} \) is fulfilled, it is safe to treat the laser source as a surface heat source. The thermal pene-
4. Effective Thermal Penetration Depth of ITO Film

tration depth is mainly determined by heat diffusion length. As discussed in the chapter 2, in nanosecond pulse length regime, the thermal penetration depth is found to be proportional to the square root of applied pulse length \[39\],

\[ l_{eff} \simeq \sqrt{2\chi\tau_p}. \quad (4.2) \]

In ultra-short pulse duration regime, the situation is more complex because the photon-electron and electron-electron coupling time is on the same order of pulse length, where electron scattering plays a dominate role in the transportation of heat and phonon-phonon coupling could be neglected. Therefore, the thermal penetration depth in such time scales is mainly controlled by the electrons, which can be calculated in case of surface lattice melting occurs for metals based on TTM model in equation 2.14, rewritten as \[41\]:

\[ l_{eff} = \left( \frac{128}{\pi} \right)^{1/8} \left( \frac{k_B^2 C_i}{C_0 T_m g^2} \right)^{1/4}. \quad (4.3) \]

However, for wide-bandgap semiconductor materials which have large optical penetration depth at the pulse wavelength, where \( l_{opt} \gg l_{th} \) is found, the absorption of laser energy has to be regarded as a volume heat source. The thermal penetration depth has to take both optical penetration depth and thermal diffusion length into consideration. In this case it is difficult to obtain an explicit mathematical expression from theoretical equations. In reference \[67\], the authors investigated heat impact depth over the laser pulse duration in short pulse regime. A thermal confinement volume is defined, within where the energy gained from the laser irradiation is higher than the thermal conduction losses. They found the growing of the thermal confinement volume is proportional to the optical penetration depth and the applied pulse duration in depth dimension. It becomes even more complicated in ultra-short pulse ablation of such material because of the nonlinear laser absorption process. Both optical penetration depth and heat diffusion length can be dependent on the laser energy intensity in ultra-short pulse regime.
4. Effective Thermal Penetration Depth of ITO Film

Figure 4.1: Schematical illustration of ablation threshold fluence for metals and semiconductors in different pulse length regime. For short pulse ablation, a $\tau_{p}^{1/2}$ scaling rule is determined. In ultra-short regime, the threshold fluence exhibits a constant value for metals but a nonlinear feature for semiconductors.

The relation of the thermal penetration depth and the pulse length can be determined by the damage threshold fluence versus pulse length experiments. For short pulse a $\tau_{p}^{1/2}$ scaling rule is found for both metals and semiconductors. In ultra-short pulse regime, the ablation threshold remains almost constant for metals, but a nonlinear feature is observed for semiconductors, schematically shown in figure 4.1 [4]. A characteristic time $\tau_c$ can be defined, which distinguishes the different dependence of the ablation threshold fluence on the pulse length and separates the short and ultra-short pulse regimes, as defined in equation 2.20 [41]. In bulk material ablation, the laser-induced heat freely conducts in spatial dimensions in the target solid. The heat diffusion length is mainly determined by a critical temporal variable, such as the pulse width. The significance of the characteristic time $\tau_c$ is that it separates the short and ultra-short pulse regimes in laser ablation.

However, when film-substrate system is concerned, the heat diffusion is affected by the film thickness in the spatial field. The film thickness could affect the temperature distribution for a specific pulse width. If the film thickness is smaller than the effective thermal penetration depth $l_{eff}$, the influence from the
substrate has to be considered.

4.2 Ablation Films with Different Thickness

The influence of film thickness on the ablation of metal films has been studied for different pulse length regimes [68–71]. Figures 4.2 and 4.3 show the examples of picosecond laser ablation of tungsten film on silicon substrate by 1064 nm wavelength pulses. The spot sizes by single pulse ablation for different film thicknesses are illustrated in figure 4.2. A well-defined linear dependence in semi-log plot can be observed with an almost constant slope for all cases. From the figure one can see that more pulse energy is required to obtain the same ablation spot size for thicker films. Figure 4.3 shows the dependence of ablation threshold on film thickness. The variation trend of the ablation threshold fluence $F_{th}$ follows the change of film thickness $d$ can be divided into two regimes. For films below a thickness of $\sim 95 \ \text{nm}$, the thresholds increase with thickness. For the films thicker than $\sim 95 \ \text{nm}$, the ablation threshold remains constant and maintains the bulk ablation threshold value. The effective thermal penetration length can be determined to be $l_{eff} \sim 95 \ \text{nm}$, which separates the film and bulk ablation features for tungsten for the picosecond pulse here.

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 consideration, a third regime can be observed. As shown in reference [72] 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. For tungsten, the optical penetration depth at 1064 nm $l_{opt} \sim 22 \ \text{nm}$ ($\delta = 4.5 \times 10^5/\text{cm}$). In summary, the threshold as a function of film thickness can divide into three regimes for metals. It starts to decrease with the film thickness. When it exceeds the optical penetration depth it increases with the rising of the thickness and finally exhibits as
4. Effective Thermal Penetration Depth of ITO Film

a constant like ablation of bulk material if the film thickness reaches the effective thermal penetration depth. Consequently it is reasonable to express ablation threshold dependence on film thickness as the plotted solid curve shown in figure 4.3. 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 \( l_{th} \gg l_{opt} \) is fulfilled.

Figure 4.2: Ablation spot size increases as the rising of pulse energy for tungsten films induced by 10 ps laser pulses at 1064 nm.

Based on the behavior of highly absorbing materials, we investigated the ablation of transparent ITO films on glass substrate for different film thicknesses. Figure 4.4 shows the ablation spots size change as the rising of applied single pulse energy. A well-defined linear dependence in semi-log plot can be observed with almost a constant slope for all cases. More energy is required for thinner film ablation to obtain the same ablation spot size compared to thicker ones. Figure 4.5 illustrates the ablation threshold fluence variation as the increase of film thickness for femtosecond and picosecond pulses ablation. The dependence of the ablation threshold fluence \( F_{th} \) on the film thickness \( d \) for ITO film demonstrates two regimes, different to the metals where three regimes are distinguished. For a thinner film, the ablation threshold fluence decreases as the film thickness
4. Effective Thermal Penetration Depth of ITO Film

increases, similar to the case of metals when its thickness is in the range of optical penetration depth [72]. The decreasing trend alters when the film thickness exceeds a certain value, where the effective thermal penetration depth of ITO is defined. Afterwards it behaves as a constant value similar to ablation of bulk material. The same trend can be found for low absorption polymer films [73]. The optical penetration depth of ITO is \( l_{opt} \sim 2\mu m \) at 1064 nm wavelength by taking linear absorption part \( (\delta = 5.3 \times 10^3/cm) \) into account. Whereas the thermal diffusion length is \( l_{th} \sim 15nm \) is calculated by \( \sqrt{2\chi T_p} \) for 10 ps pulse length irradiation. The difference from metals is found that \( l_{opt} \gg l_{th} \) for such low absorption ITO films.

### 4.3 Theory Analysis of Thermal Penetration Depth

In order to describe the dependence of the threshold fluence on film thickness, we assume a purely thermal origin of the observed ablation effects. Regarding

![Figure 4.3: Dependence of ablation threshold fluence on film thickness for tungsten obtained by 10 ps laser pulses at 1064 nm. The solid line is plotted according to the theoretical prediction.](image)
the film temperature reaching its melting point as the criterion for ablation. Neglecting the lateral heat diffusion and only considering the depth dimension due to the large beam size, the temperature rises in the heated volume due to

Figure 4.4: Ablation spots size increases as the rising of pulse energy for ITO films induced by 10 ps pulses at 1064 nm.

Figure 4.5: Dependence of threshold fluence on the film thickness of ITO ablated by 10 ps pulses at 1064 nm and 150 fs pulses at 800 nm.
4. Effective Thermal Penetration Depth of ITO Film

the absorption of laser energy can be expressed as [69]:

\[ \Delta T_m = \Delta Q/C, \]  \hspace{1cm} (4.4)

where \( \Delta Q \) is the total absorbed energy and \( C \) is the heat capacity at constant pressure.

![Figure 4.6: Laser-induced heat transportation and the energy balance analysis in film-substrate system.](image)

In case the heat loss to the substrate has to be taken into consideration, the laser-induced heat transportation and the energy balance analysis is schematical demonstrate in figure 4.6, where \( Q_a \) stands for the total absorbed laser energy by the film, \( Q_f \) is the energy required for the film to reach its melting point and \( Q_s \) is the energy maintained by the substrate. \( \Delta T_m \) is the temperature increase needed for melting, which is a constant for specific material. \( \rho, c \) are the mass density and specific heat, \( l_{th} \) stands for the heat diffusion length, where the subscript \( f \) 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.
The conservation of energy is easily obtained as:

\[ Q_a = Q_f + Q_s \]  \hspace{1cm} (4.5)

where

\[ Q_a = \frac{F_a}{2}(1 - e^{-\delta d})(1 - R), \]
\[ Q_f = \frac{1}{2}T_c \rho_f \cdot \left( 1 + \frac{l_{th,f} - L_f}{l_{th,f}} \right) L_f, \]  \hspace{1cm} (4.6)
\[ Q_s = \frac{1}{2}T_c \rho_s \cdot \left( \frac{l_{th,f} - L_f}{l_{th,f}} \right) l_{th,s}. \]

From equations 4.5-4.6, a uniform model for threshold fluence of melting can be obtained on condition \( Q_f \geq \Omega \), written in the form:

\[ F_{th} \simeq \frac{T_m}{(1 - e^{-\delta d})(1 - R)} \left[ \left( \rho_f c_f - \left( \frac{l_{th,s}}{l_{th,f}} \right) \rho_s c_s \right) L_f + l_{th,s} \rho_s c_s \right]. \]  \hspace{1cm} (4.7)

From this equation the different regimes of ablation threshold variation trends for metal and transparent ITO films can be identified. As illustrated in figure 4.7, the ablation threshold dependents on film thickness is simulated according to the equation 4.7 for metal and ITO films on glass substrates.

For metal films, \( l_{opt} \ll l_{th} \). As shown in figure 4.7(a), the ablation threshold dependence on the film thickness can be characterized in three regimes:

- In the first regime I, \( d \ll l_{opt} \ll l_{eff} \) and \( L_f = d \) are fulfilled. For small \( d \) in the equation 4.7, the limit in the first item on the right is found to be:

\[ \lim_{d \to 0} \frac{d}{1 - e^{-\delta d}} = \frac{1}{\delta}. \]  \hspace{1cm} (4.8)

However, for the second item which defines the influence of the substrate, the limit goes to infinity due to \((1 - e^{-\delta d}) \sim 0\) 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 its melting temperature,
4. Effective Thermal Penetration Depth of ITO Film

\( F_{th} \sim 1/d \) is found.

- In the second regime II, \( l_{opt} \ll d \ll l_{eff} \) and \( L_f = d \) are fulfilled. In this case the pulse energy is regarded to be totally absorbed, where the item \((1 - e^{-\delta d}) \sim 1\). The influence from the substrate is limited. Therefore one can find \( F_{th} \sim d \) is established.

- In the third regime III, \( l_{opt} \ll l_{eff} \ll d \) and \( L_f = l_{eff} \) are fulfilled. The laser energy is regarded to be totally absorbed and the heat volume is limited by \( l_{eff} \). The influence from the substrate is neglected. Hence the ablation threshold \( F_{th} \) is no longer dependent on the film thickness, but behaves as ablation of bulk material.

For transparent ITO films, \( l_{opt} \gg l_{th} \). As shown in figure 4.7(b), the ablation threshold dependence on film thickness can be characterized in two regimes:

- In the first regime I, \( d \ll l_{eff} \ll l_{opt} \) and \( L_f = d \) are fulfilled. Similar to the case of metal films in regime I, the substrate influence plays a dominant role on ablation threshold fluence. \( F_{th} \) decreases with the rising of film thickness.

- In the second regime II, \( l_{eff} \ll d \) and \( L_f = l_{eff} \) are fulfilled. Because of the large optical penetration depth \( l_{opt} \), the changing of the film thickness \( d \) in this regime only leads to a small variation of \((1 - e^{-\delta d})\) item, which can be approximately regarded as a constant. On the other hand, the heat volume is controlled by \( l_{eff} \) which is independent on the film thickness \( d \). Therefore \( F_{th} \) approximately remains constant.

It has be mentioned that the effective thermal penetration depth \( l_{eff} \) is a co-effect of the optical penetration and the thermal diffusion. For metals, due the small optical penetration depth, the thermal penetration is mainly contributed by the heat diffusion, where \( l_{eff} \sim l_{th} \) is fulfilled. In ultra-short pulse regime, \( l_{opt} \) has to be taken as electron diffusion length instead. For ITO material, the
4. Effective Thermal Penetration Depth of ITO Film

Figure 4.7: Simulation results of threshold fluences dependent on the thickness for metal and transparent ITO films.

The effective thermal penetration depth $l_{ef}$ is about 100 nm for picosecond laser and about 85 nm for femtosecond laser in our experiments, which are both larger than the thermal diffusion length $l_{th}$ of $\sim 15\text{nm}$ by 10 ps and $\sim 1\text{nm}$ by 150 fs, but smaller than the optical penetration depth $l_{opt}$ of $\sim 1\mu\text{m}$ order calculated by the linear absorption part. However, it is complicated to give an analytical expression for $l_{ef}$, especially for large optical penetration materials. From the threshold $F_{th}$ dependent on the film thickness $d$ experiments, the effective thermal penetration depth $l_{ef}$ can be determined and different ablation characteristic features can be identified.

4.4 Effective Thermal Penetration Depth Influence on Ablation

In selective laser ablation of thin films, generally weak absorption of the substrate to the applied pulse compared to the film absorption is fulfilled. In this case the film can be removed by both front- and rear-side irradiation. For example, in P1 step which is often the laser ablation of the TCO layer in thin film solar cell manufacturing shown in figure 1.3, some authors advised that rear-side ablation
can achieve better ablation qualities based on experimental studies \[74,75\]. Here we investigated the thermal penetration depth influence on the ablation of ITO films by front- and rear-side irradiation. Figure 4.8 schematically shows the different irradiation methods. The optical penetration depth, the thermal penetration depth and the film thickness are also illustrated.

Previous works already demonstrated that the different ablation geometry could happen for laser ablation of metals by front- and rear-side irradiation, when the film thickness exceeds the thermal penetration depth \[76,77\]. The film thickness is crucial in determining the amount of energy guided to the substrate. If the film thickness is smaller than the thermal penetration length, the temperature field can be regarded as the same for both irradiation directions. On the other hand, if the film thickness is larger than the thermal penetration length, the influence from the substrate can be neglected for front-side ablation. Hence, the temperature distribution induced by laser irradiation from the front- or rear-side ablation could make a strong difference and alter the surface ablation morphology. Figure 4.9 demonstrates the numerical simulation results of the thermal distribution when the peak temperature is obtained over the time for the film thickness more than the thermal penetration depth. One can detect a significant difference in the thermal distribution for front- and rear-side irradiation.
4. Effective Thermal Penetration Depth of ITO Film

Figure 4.9: Numerical simulation results of temperature distribution induced by laser irradiation from (a). front-side, and (b). rear-side. The location marked by “x” denotes the maximum temperature point when the peak temperature is obtained over the time.

The images listed in figures 4.10, 4.11 and 4.12 are the single-pulse ablation results of transparent ITO films of 50 nm and 100 nm thickness on glass substrates, which are irradiated by 300 ms, 10 ps and 150 fs laser pulses from front- and rear-side. The result in each case is achieved with the same laser fluence level for front- and rear-side ablation. For the 300 ms pulse ablation, the film is seriously cracked for both thicknesses due to the large laser induced thermal stress. The ablation spot geometries do not show so much difference due to the large thermal penetration depth at this pulse duration. For 10 ps and 150 fs pulse ablation, the films are likely to be removed by thermal melting and vaporization without film cracking. No apparent ablation geometry difference can be found for small thickness films, demonstrated by the 50 nm film results. But for the thickness of 100 nm films, much cleaner and clearer ablation spots can be obtained by rear-side ablation. The figures reveal that the ablation quality could demonstrate a visible difference for those film thicknesses exceeding the thermal penetration depth demonstrated by 10 ps and 150 fs pulse ablation of
100 nm ITO films. Actually rear-side selective patterning of ITO for solar cell applications is extensively adopted in industrial production.

The thermal penetration depths of ITO film on glass substrate are determined by $F_{th}$ versus $d$ experiments for different pulse lengths, shown in Figure 4.13. For comparison both front- and rear-side irradiation are conducted. For different pulse length, the thermal penetration depth is found to be changed consistent

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Figure 4.10: Laser ablation geometry of ITO films from front- and rear-side irradiation by 300 ms pulse with 1064 nm wavelength.
4. Effective Thermal Penetration Depth of ITO Film

with the results shown in figure 4.1, where a linear dependency can be defined for short pulses but nonlinear dependency is observed for ultra-short pulses. The conclusion for both metal and ITO materials are schematically shown in figure 4.14, where the film and bulk ablation features can be separated by the thermal penetration depth. Concerning the results from front- or rear-side ablation, the threshold fluence curves are observed to be separated when the film thickness ex-

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Figure 4.11: Laser ablation geometry of ITO films from front- and rear-side irradiation by 10 ps pulse with 1064 nm wavelength.
4. Effective Thermal Penetration Depth of ITO Film

ceeds the thermal penetration depth, where rear-side ablation is slightly increased compared to the constant value for front-side ablation, schematically shown in figure 4.15. In case of long pulse irradiation, or for thin films, the ablation does not demonstrate so much difference in threshold fluence and spot morphology. On the contrary, by applying ultra-short laser pulses or using relatively thick films, the ablation threshold fluence is slightly higher by rear-side than the one

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Figure 4.12: Laser ablation geometry of ITO films from front- and rear-side irradiation by 150 fs pulse with 800 nm wavelength.
obtained front-side. Also, the ablation spots show much better rim performance by rear-side irradiation in the studied 100 nm thick ITO films.

Figure 4.13: The ablation threshold fluence of ITO films changes as the function of the film thickness by different pulse length of 300 ms (top), 10 ps pulse (middle) and 150 fs (bottom). Both front- and rear-side irradiations are presented.
4. Effective Thermal Penetration Depth of ITO Film

4.5 Conclusion

In this chapter 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 a surface heat source. Due to the

Figure 4.14: Schematic demonstration of laser ablation threshold as a function of film thickness for (a) metal and (b) ITO films for different pulse lengths. \( l_{\text{eff}} \) indicates the thermal penetration length which differentiates the film and bulk solid features for laser ablation. Note that the results were obtained by laser front-side irradiation. The variation of \( l_{\text{eff}} \) is found to be consistent to the result in figure 4.1.

Figure 4.15: Ablation threshold as a function of film thickness for front- and rear-side irradiation. The ablation threshold curves separate when the film thickness exceeds the thermal penetration depth.
4. Effective Thermal Penetration Depth of ITO Film

complicated nonlinear absorption of laser pulses for transparent semiconductors, theoretical prediction of thermal penetration depth is difficult. By experimentally getting the relation between ablation threshold fluence and the film thickness, the effective thermal penetration depth for both metal and ITO films can be obtained. We discussed the ablation of ITO films from front- and rear-side ablation based on the influence from the effective thermal penetration depth. The results show that the ablation geometry exhibits differences when the film thickness exceeds the effective thermal penetration depth.
Chapter 5

Incubation Effect on Laser Ablation of ITO Film

This chapter will present the ablation of ITO thin films on glass substrate induced by single- and multi-pulse laser irradiation. For multi-pulse ablation, the incubation effect results in a reduction of the damage threshold, especially apparent at low pulse numbers and in very small film thicknesses. The incubation effect dependent on the film thickness will be investigated. The incubation effect influence on the laser patterning structure of ITO films is exhibited while increasing the pulse overlapping rate. The width of the patterned line can be predicted by the proposed model involving the laser fluence, the overlapping rate and the incubation coefficient.

5.1 Introduction

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 “N-on-one” accumulation effect. The incubation phenomena have been observed in various materials processed by pulsed lasers, including polymers [78,79], metals [80,81], semiconductors [82] and insulators [83].
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The origin of the incubation is not yet fully revealed. For example, in UV laser processing of PMMA, some authors argued that the incubation was associated with the buildup of pressure due to the formation of polymer fragmentation [84–89]. On the contrary, Küper and Stuke showed that the incubation of PMMA with 248 nm laser was attributed to the photochemical degradation and mechanical stability reduction by means of spectroscopy studies [78, 79]. Graciela and co-workers suggested that the decomposition of PMMA by UV incubation pulses was the result of photoinduced formation of defect centers, which enhanced the absorption of UV light [90]. From their calculation, the ablation threshold is associated with the pulse number by:

\[
F_{th}(1) = F_{th}(N)[1 + kF_{th}(N)(N - 1)],
\]

(5.1)

where \(F_{th}(1)\) and \(F_{th}(N)\) are the single-shot and N-shot damage thresholds, respectively. Coefficient \(k\) reflects the incubation, which is the function of absorption cross section of PMMA (\(\sigma\)) and the absorption cross section of the induced defect center (\(\beta\)). Based on equation 5.1 the authors successfully obtained the value of \(\sigma\) and \(\beta\) [90].

For metals, it was reported that for multi-pulse laser induced damage by 10 ns Nd:YAG laser pulses with 1064 nm wavelength, the accumulation process was attributed to thermal stress-strain energy storage [80]. The authors argued that multi-pulse laser ablation on a site was similar to the bulk mechanical fatigue damage. On the analogy of the fatigue failure induced by the stress for \(N\) cycles, the authors derived a cumulative equation:

\[
F_{th}(N) = F_{th}(1)N^{S-1},
\]

(5.2)

where \(S\) is so called incubation coefficient which quantifies the degree of incubational behavior. The model gives a reasonable interpretation for the incubation behavior of metals for the reported experiments in many research works [91, 92].
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It is also appropriate to fit the experimental data in pulsed laser ablation of some semiconductors [82]. It also appears in evaluation of the incubation effect in femto- and nanosecond laser ablation of doped PMMA conducted by Krüger et. al. [93].

For dielectric or some semiconductor materials with “N-on-one” irradiation, the incubation effect can be attributed to laser induced defects. Multi-shot irradiation onto a site of dielectrics could induce the generation of point defects by multi-photon excitation, for example formation of color centers [94, 95]. The strength of such an accumulation process is related to the excitation and generation of electrons initiated by combined multi-photon and avalanche ionization. The threshold fades due to the decrease of defect accumulation for increasing $N$ until it reaches a constant level. Therefore, a different equation was proposed for this case [96]:

$$F_{th}(N) = F_{th}(\infty) + [F_{th}(1) - F_{th}(\infty)]e^{-k(N-1)}, \quad (5.3)$$

where $F_{th}(\infty)$ gives the maximum fluence at which the material could be permanently irradiated without causing damage, $k$ is the factor characterizing the incubation degree. In this case the ablation threshold drops dramatically at low pulse numbers and remains constant for a large number of pulses. This dependency is mainly used in laser processing of dielectric materials [97].

Equation 5.2 is only valid for a limited number of pulses since the threshold fluence cannot decrease to zero [91]. On the other hand it is also not definitely applicable to all experiments dealing with metals. An exception has been described by C. Kern et. al. in their experiment on femtosecond laser-induced damage of thin Au films [98]. They adopted equation 5.3 to fit the multi-shot damage threshold versus the pulse numbers and argued that surface modification is responsible for incubation for films significantly thinner than the characteristic penetration depth [81].

In this chapter we investigate the incubation behavior of the wide band-gap
5. Incubation Effect on Laser Ablation of ITO Film

semiconductor ITO material when exposed to picosecond laser pulses. Structuring of ITO films has a great impetus from industrial applications. Accordingly, laser patterning of ITO thin films on glass substrates has been extensively studied with various pulsed laser sources [18–25, 27, 99–104]. However, a detailed study of the incubation behavior of ITO films and its influence on laser patterning has not yet been reported. Here we will show the decline of ablation thresholds as a function of the pulse number and investigate the incubation coefficient as well as its dependence on film thickness and its influence on laser line patterning of thin ITO films.

5.2 Incubation Effect in Multi-pulse Ablation

5.2.1 Incubation of ITO films

Figure 5.1 illustrates the typical surface damage morphologies of ITO films irradiated by different numbers of laser shots recorded by SEM. The laser fluence was set to 1.33 J/cm², slightly above the single-shot threshold. By increasing the number of incident laser pulses the damaged site area grows and the rims are getting sharper. Figure 5.2 demonstrates the surface damage morphologies induced by different laser fluences with a fixed number of laser shots (N = 10). Increasing the laser fluence will enlarge the ablation area, which is basically the same effect as increasing the number of laser pulses.

To determine the damage thresholds of ITO films as a function of the incident pulse number, as well as its dependence on film thickness, a series of experiments was performed with different laser fluence levels on samples with thicknesses of 10 nm, 50 nm and 205 nm. Figure 5.3 presents the relationships of measured squared diameter plotted against the logarithm of the applied pulse energy for N = 1, 100 and 1000 laser pulses, respectively. From the data plots, a well-defined linear dependence in semi-log plot can be observed with an almost constant slope for all cases which yields a beam radius of about 20 µm. In all plots, for the same pulse
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energy, the ablation site is bigger for thicker films, especially for lower pulse shots. As the pulse number has been further increased to 1000, the ablation site area changes almost similar for the three film thicknesses. This effect can be reflected from the calculated damage thresholds. For a 1 pulse shot, the damage thresholds are 1.48 J/cm$^2$, 0.89 J/cm$^2$ and 0.35 J/cm$^2$ for 10 nm, 50 nm and 205 nm films, respectively. On the contrary, for 1000 pulse shots, the threshold values become 0.36 J/cm$^2$, 0.26 J/cm$^2$ and 0.25 J/cm$^2$. In this case the differences between the three thicknesses are getting much smaller in terms of ablation thresholds. This implies for a large pulse number that the damage threshold is nearly independent on the film thickness. Another result one can observe is that the thinner ITO

![Figure 5.1: Laser induced damage micro morphologies of the ITO films irradiated by different pulse numbers recorded by SEM, where (a) 1 pulse, (b) 10 pulses and (c) 100 pulses. The applied laser fluence was 0.83 J/cm$^2$. The film thickness was 100 nm for all cases.](image1)

![Figure 5.2: Laser induced damage micro morphologies of the ITO films irradiated by different pulse energies recorded by SEM, where (a) 0.53 J/cm$^2$, (b) 0.88 J/cm$^2$ and (c) 1.33 J/cm$^2$. The applied pulse number was 10. The film thickness was 100 nm for all cases.](image2)
5. **Incubation Effect on Laser Ablation of ITO Film**

Film with lower pulse shots yields higher damage thresholds, which however, drops faster with an increasing number of laser shots. This is contrary to the metal films where the ablation thresholds decrease when the film thicknesses get thinner if it is in the range of the thermal penetration penetration length \[105\].

It has to be mentioned that for multi-pulse shots, the delay between two neighboring pulses in our experiments is 5 \(\mu s\), which is much longer than all relaxation times of electrons and phonons, in the range below 10 \(ps\) \[106\].

The threshold fluence versus the number of applied pulses is shown in figure 5.4. It is obvious that the threshold fluence drops strongly when the surface is exposed more than once with otherwise identical laser parameters. Especially for thinner films, the damage threshold drops dramatically when increasing the number of pulses. For thicker films, a less pronounced drop can be observed, only apparent for a low number of laser pulses. For example, at 1 shot and 1000 shots, for a thickness of only 10 \(nm\) the ablation threshold drops by 75\% but only by 30\% in the case of a 205 \(nm\) film thickness. These observations indicate that for very thin films and only a few pulses, a strong cumulative effect occurs. As also shown in figure 5.4, the thresholds will drop with an increasing number of incident pulses. However, beyond a specific number of pulses the fluence threshold remains constant. The threshold value turned to its final value with less pulses for thick films, e.g. for a thickness of 205 \(nm\) the characteristic value for laser pulses is about 10, whereas for 50 \(nm\) thick films the threshold falls within the first 100 pulses. Therefore, it is reasonable to exclude the points in figure 5.4 which have reached the final threshold value for high pulse numbers \[91\]. The relationship between threshold and pulse number can be quantitatively expressed by equation 5.2, as indicated by the dotted lines in figure 5.4. It is interesting to see that the linear fitting lines yield the same slope values of -0.18, although there is a high uncertainty for the 205 \(nm\) thickness due to a lack of enough experimental data. This is justified to conclude that the incubation effect is attributed to the surface stress-strain energy storage by the linear relationship in the logarithmic plot of the damage thresholds against the incident pulses number, yielded by
5. Incubation Effect on Laser Ablation of ITO Film

Figure 5.3: The measured squared diameter of ablated spots plotted against the applied pulse energy, where 1 shot (top) 100 shots (middle) and 1000 shots (bottom).

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5. Incubation Effect on Laser Ablation of ITO Film

Figure 5.4: In a logarithmic plot the ablation thresholds decrease almost linearly over the number of pulses. The lines are a fit to equation 5.2 with only the filled data points are used in the fit. A fixed slope is applied and the incubation coefficient can be estimated to $S = 0.82$.

equation 5.2. The incubation coefficient can be calculated to $S = 0.82$.

5.2.2 Comparison with metal films

As mentioned in the last chapter, the dependency of the threshold fluences on the film thickness is different for metals and ITO materials. The same conclusion can be obtained here. For metal films, the ablation threshold fluence is found to increase as the rising of film thickness in the range of thermal penetration depth, when same pulse number is applied. For ITO films, the inverted trends can be defined, where the ablation threshold is found to decrease with the rising of thickness. The interesting thing can be found with the comparison of the incubation effect dependent on the film thickness. Different variation trends can be defined for both type of films as well.

Usually the storage of strain-stress energy induced by multi-pulse irradiation is because of the incubation effect when talking about the ablation of thick metals. Most of published literature comes to this point of view, where equation 5.2
5. Incubation Effect on Laser Ablation of ITO Film

Figure 5.5: Ablation threshold fluence of various Au layer thicknesses in dependence of pulse number per damage site. The lines are a fit to equation 5.3, the fit parameters for an infinite number of shots on a layer of given thickness are presented in the graph.

is found to fit quite well with their experimental data [80, 81]. However, when the film becomes thinner, the dependency of the ablation threshold fluence on the pulse number changes. As shown in figure 5.5, the multi-shot damage thresholds fit quite well with equation 5.3 instead of 5.2 when the film thickness is in the range of thermal penetration depth. From their experiment, the largest differences between single and multi-shot laser induced damage occurs for the thickest layers, which gets higher cumulative effects. For thinner films that are significantly smaller than the thermal penetration depth, the strengthen of the surface modification is regarded to be responsible for incubation increases, rather than in multi-pulse ablation where the storage of strain-stress energy as the bulk metal samples [98].

For wide bandgap semiconductors, the multi pulses irradiation on a bulk solid with fluence below single pulse ablation threshold is more likely to cause the defect of the material’s band structure, for example forming color center [22]. This is considered to be the reason for the incubation effect for such semiconductors.
Therefore the equation 5.3 is regarded to be more suitable to describe the incubation effect rather than the strain-stress deformation model by equation 5.3, which can be found in several publications [22]. However, as we found in our experiment on ablation of ITO films, the strain-stress deformation model described by equation 5.2 is a better fit to the experimental data, shown in figure 6.7. Different to metal films, the largest differences between single and multi-shot laser induced damage occur for the thinner layers. It can be regarded that the behavior of the storage strain-stress energy induced by multi-pulse irradiation is responsible for the incubation effect for ITO film.

5.3 Incubation Effect on Laser Ablation Line

The discussion above was completely referred to multi-pulse shots on a single site, based on the “N-on-one” experiment. In most practical applications, however, laser patterning of lines or areas is the result of a laser pulse train with a fixed overlapped area usually determined by the laser scanning speed, laser repetition rate and the spot diameter. The overlapped area between two adjacent single-shot sites defines the overlapping rate as schematically illustrated in figure 5.7. In mathematical terms it can be expressed by

$$R_{ov} = \frac{D_1 - d}{D_1} \times 100\%, \quad 0 < d \leq D_1, \quad (5.4)$$

where $D_1$ represents the damage site diameter at a given laser fluence, $d$ is the distance between two adjacent sites calculated by $d = v/f$ with $v$ the laser scanning speed and $f$ the laser repetition rate.

Assuming there is no incubation effect, the width of the patterning line would always be equal to the diameter of the single-shot site, $L = D_N = D_1$, no matter how much overlapping rate has been used. Figure 5.7 illustrates the patterning lines with different overlapping rates at the laser fluence of 0.88 $J/cm^2$. As
5. Incubation Effect on Laser Ablation of ITO Film

one can see, the line width increases with higher overlapping rate and no longer remains equal to the diameter of a single-shot site. This indicates the significant incubation effect on the width of the patterning lines.

For further calculations we replaced the pulse number in “N-on-one” experiment by

\[ N \approx \frac{D_1}{d} = \frac{1}{1 - R_{ov}}, \]  
(5.5)

which can be considered as the effective pulse number overlapped within the single-spot site shown in figure 5.6. Combining with equation 5.2, equations 5.4 and 5.5, one can obtain

\[ L = D_1 \sqrt{1 + \frac{(S - 1)}{\ln[F/F_{th}(1)]} \ln(1 - R_{ov})}, \]  
(5.6)

with \( L \) representing the ultimate line width at a given laser fluence \( F \) and \( F_{th} \) is the single-shot ablation threshold. It is obvious, that for an overlapping rate \( R_{ov} = 0 \), i.e. no overlapped area between two succeeding pulses, incubation

Figure 5.6: Schematic diagram illustrate the definition of overlapping rate for laser patterning of lines. \( D_1 \) represents the damage site diameter at a given laser fluence, \( d \) is the distance between two adjacent sites. \( L \) represents the confined line width, \( L \geq D_1 \).
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Figure 5.7: Laser induced patterning line morphologies on the ITO films irradiated by different overlapping rates recorded by SEM, where (a) shows the results for $R_{ov} = 0$, (b) $R_{ov} = 30\%$, (c) $R_{ov} = 75\%$ and (d) $R_{ov} = 95\%$. The applied laser fluence has been $0.88 \text{ J/cm}^2$. The film thickness was $100 \text{ nm}$ for all cases.

effects disappear and the width of the line equals to $D_1$. As the overlapping rate increases, the width of the patterning line increases, as well. Assuming the other extreme case $R_{ov} = 100\%$, the width theoretically approaches infinity which is equal to the “N-on-one” case with an infinite number of pulses. However, in this situation equation 5.2 is no longer valid.

In order to verify equation 5.6, we conducted a series of experiments with 100 nm ITO films applying different overlapping rates, as plotted in figure 5.8. The incubation coefficient was evaluated in figure 5.4, where it comes to $S = 0.82$. The single-shot ablation threshold is $0.59 \text{ J/cm}^2$ and the applied laser fluence $F = 0.88 \text{ J/cm}^2$ induces a damage site diameter of $D_1 = 15.3 \mu \text{m}$. Substituting these values for the parameters in equation 5.6, the result is plotted in a solid line, as shown in figure 5.8.

The plot reveals that the equation 5.6 agrees quite well with the experimental data. A slight deviation appears at higher overlapping rates, which is equivalent to an extremely high number of incident pulses on one site and results from the failure of equation 5.2 for high values of $N$. Taking the course of the development into account, it is reasonable to generalize equation 5.6 to the laser patterning
5. Incubation Effect on Laser Ablation of ITO Film

Figure 5.8: Width of patterning lines versus different overlapping rate. The applied laser fluence has been 0.88 J/cm². The solid line is fitted according to equation 5.6.

of material with an incubation behavior which can be described by equation 5.2, for example most metals. In cases where equation 5.3 should be used to calculate $F_{th}(N)$ for multi-pulse ablation, a similar derivation course could be used to model the width of the patterning line, e.g. for most of dielectrics.

5.4 Conclusion

Picosecond laser pulsed ablation of ITO thin film using 1064 nm wavelength was conducted in this paper. The single-shot damage threshold was found to increase as the film thickness gets thinner, which is opposed to the behavior of metals. Multi-pulse ablation exhibited an incubation effect which is attributed to the accumulation of plastic deformation. The incubation coefficient $S = 0.82$ was obtained by approximation and turned out to be independent of the film thickness, at least in the range of the film thickness between 10 nm and 100 nm. A simple mathematical model describing the influence of the incubation effect during laser patterning of ITO has been developed, which allows the prediction of the width
5. Incubation Effect on Laser Ablation of ITO Film

of patterning lines with varying overlapping rates between two succeeding pulses. The results can be transferred to the laser patterning of any material obeying an incubation expressed by $F_{th}(N) = F_{th}(1)N^{S-1}$.
Chapter 6

Laser Ablation of ITO Film on PET Substrate

In this chapter, the fundamental removal mechanisms of laser selective ablation of ITO films on glass and PET substrates will be investigated. In order to selectively pattern ITO films from a substrate, understanding the ablation mechanisms is critical. Either thermal melting, evaporation or solid thermo-mechanical cracking, delamination processes could be involved via the parametric study, depending on the properties of the substrate and the parameters applied to the laser pulse. The optimization of processing parameters for picosecond laser selective pattern of ITO layer from flexible PET substrates is conducted based on the mechanical stress model.

6.1 Introduction

Laser direct patterning of ITO conductive thin film on glass substrate has been well established in some fields of industry [101,107–110]. Laser patterning of ITO on flexible polymers has received less attention so far. Chen et. al. compared the laser scribing and patterning of ITO thin films deposited on glass and plastic substrate with top-hat intensity beams [26]. Tsai et. al. used a 248 nm excimer laser to pattern ITO on polyethylene terephthalate (PET) substrates [111]. The
results of the patterned ITO showed re-solidified melt ridges at the edge, hence they suggested it is a thermal evaporation process. Willis et. al. used time resolved laser diagnostics technology when studying the laser ablation of ITO from PET substrate by 1064 nm laser with nanosecond pulses. The authors presented that the removal of ITO on PET was a solid phase delamination process rather than by a melting and evaporation process [58].

It is apparent that the removal of the ITO film can be a result of different mechanisms, either thermal evaporation or mechanical stress processes. Systematic studies on the dependence of the laser ablation mechanism on the substrate and the laser pulse setting is required, especially for the flexible substrate due to the increasing application of flexible electronics. Laser selective patterning of ITO films on flexible substrates is a prospective method in assistant fabrication of these devices.

### 6.2 Thermal Stress in Ablation of Film-substrate System

As mentioned, laser irradiation on a solid target will result in the temperature increasing accompanied with generation of mechanical stress. Generally, for bulk solid material it is more likely to be removed by thermal effects. However, several pieces of experiments evidence that under certain conditions photomechanical effects could play a main role in laser ablation, for example in tissue ablation [112] the material can be removed with pulse fluence lower than the evaporation threshold. In ablation of film-substrate samples, the mechanical stress could play more important role when huge mismatch of the physical properties for the two mediums occurs. For example, the misfit of thermal expansion could enhance the stress amplitude. Also the mismatch of the acoustic velocity in the different mediums leads to a considerable energy deposition at the layer interface due to the reflection of stress wave. This could lead to either film cracking or mechani-
Theoretical, by treating laser pulse as a classic transient heat source, according to the absorption ability of the film and substrate, the considered system can be described by classic heat diffusion equation 2.3 and thermo-mechanical equations. In polar coordination the temperature increase due to laser irradiation can be described by:

$$\rho C \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (k \frac{\partial T}{\partial r}) + \frac{\partial}{\partial z} (k \frac{\partial T}{\partial z}) + S,$$

(6.1)

where $S$ represents the laser heat source. Here we take the linear absorption as the main consideration. Assuming the material absorption of laser pulse has a Gaussian temporal and spatial profile expressed as [113]:

$$S(r, z, t) = \frac{2}{\tau_p} \sqrt{\frac{\ln 2}{\pi}} \delta \exp \left[ -4 \ln 2 \left( \frac{t}{\tau_p} \right)^2 \right] \exp(-\delta z) \exp \left[ -\left( \frac{r}{\omega_0} \right)^2 \right].$$

(6.2)

The equation 6.1 is used by several groups in calculation of the surface temperature of ITO film by laser irradiation [18, 19, 25, 26]. It is confirmed through the calculation that the maximum surface temperature exceeds the evaporation point of ITO material by nanosecond pulse when the fluence is above the ablation threshold.

On the other hand, the stress generation by laser is mainly attributed to the thermal expansion before the formation of plasma by high pulse intensity irradiation. The constitutive relation of the stress-strain due to temperature rise $\Delta T$ can be written as [114]:

$$\{\sigma\} = [D]\{\epsilon\} - \{m\} \Delta T,$$

(6.3)

where $[D]$ is the elasticity matrix, $\{\sigma\}$ is the stress vector and $\{\epsilon\}$ is the strain
6. Laser Ablation of ITO Film on PET Substrate

vector. The expressions for \( \{\sigma\}, \{\epsilon\}, \{m\} \) and \([D]\),

\[
\{\sigma\}^T = \{\sigma_{rr}, \sigma_{\theta\theta}, \sigma_{zz}, \sigma_{rz}\},
\{\epsilon\}^T = \{\epsilon_{rr}, \epsilon_{\theta\theta}, \epsilon_{zz}, \epsilon_{rz}\},
\{m\} = \begin{pmatrix}
1 \\
1 \\
1 \\
0
\end{pmatrix} \begin{pmatrix}
E\alpha \\
\frac{E}{1-2\nu}
\end{pmatrix},
\]

\[
[D] = \frac{E}{(1+\nu)(1-2\nu)} \begin{pmatrix}
1 - \nu & \nu & \nu & 0 \\
\nu & 1 - \nu & \nu & 0 \\
\nu & \nu & 1 - \nu & 0 \\
0 & 0 & 0 & (1-2\nu)/2
\end{pmatrix}.
\]

Here \( E \) is the Young’s Modulus, \( \nu \) is Poisson’s Ratio and \( \alpha \) is the thermal expansion coefficient. In equation 6.3, the first item stands for the stress relaxation due to the material expansion, the second item indicates the stress generation from the temperature rising. The balanced force equations in a medium can be expressed as follows [115]:

\[
\frac{\partial \sigma_{rr}}{\partial r} + \frac{\partial \sigma_{rz}}{\partial z} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} = 0,
\frac{\partial \sigma_{rz}}{\partial r} + \frac{\partial \sigma_{zz}}{\partial z} + \frac{\partial \sigma_{rz}}{\partial r} = 0,
\]

(6.5)

where \( \sigma_{rr}, \sigma_{\theta\theta} \) and \( \sigma_{zz} \) are normal stresses and \( \sigma_{rz} \) is the shear stress. The volume expansion of the material is described by the node displacements, \( u \) in radial direction and \( w \) in \( z \) direction. The strains-displacement relation is described as:

\[
\epsilon_{rr} = \frac{\partial u}{\partial r}, \epsilon_{\theta\theta} = \frac{u}{r}, \epsilon_{zz} = \frac{\partial w}{\partial z}, \epsilon_{rz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}.
\]

(6.6)

Assuming no material deformation occurs, where \( u = w = 0 \), an approximate
solution to estimate the film stress induced by a constant temperature difference \( \Delta T \) can be obtained solely by the second item:

\[
\sigma_{rr} = \frac{E\alpha\Delta T}{1-2\nu}.
\]  

(6.7)

Equation 6.7 appeared in several publications to estimate the stress in the film [5, 58, 116]. In reference [58] the authors used equation 6.7 to calculate the stress energy in nanosecond laser processing of ITO film on PET substrate. If the thermal stress exceeded the cohesive and adhesive strength between the film and substrate, the film will be removed from the substrate. The stored stress energy converts to the kinetic energy of the ejected fragments. Based on the author’s calculation, the calculated velocity of the fragments were very close to the value measured by shadowgraph images.

The dynamic temperature, displacement and stress in equations 6.5-6.6 can be solved by using the finite-element method (FEM). In reference [117], the authors demonstrate the predictive numerical FEM simulation of the laser scribing of SnO\(_2\): F thin film on glass by laser irradiation. The dynamic subsequently-coupled thermo-mechanical model analysis shows that SnO\(_2\): F film gets tensile stress due to the glass thermal expansion by heat conduction during the film cooling period. Tensile stress caused the damage of SnO\(_2\): F layer even when the laser fluence is lower than the melting threshold. Another example can be found in femtosecond laser pulse irradiation on thin gold film on glass. The dynamic thermo-mechanical model has been successfully used to simulate the formation of micro-bumps observed in experiments [118].
6.3 Parametric Study of Laser Ablation of ITO Film

6.3.1 Pulse length effect

Experiments with different laser pulse width were applied to ablation of ITO film on glass substrate. Here we would like to present the mechanical stress influence induced by lasers with different pulse widths. The glass substrate is basically transparent at 1064 nm wavelength. Consequently, laser heating is generated in the ITO film where the substrate acts as a thermal barrier due to relatively low thermal conductivity. The glass substrate constrains the deformation of the upper ITO layer due to contact at the interface.

Figure 6.1(a) shows the single-pulse ablation geometries of ITO film by 300 ms pulses by increasing the laser incident fluences. The irradiated area is modified respective to the virgin ITO film observed from the color change in optical microscopy. The laser irradiation causes serious film cracking and part delamination in solid phase with relatively low pulse energy. By increasing the applied laser fluence, the number of cracking channels increases and part of the film is punched out from the substrate. However, it is difficult to totally remove the layer in the irradiation area. The substrate gets damaged at high laser fluence. No suitable pulse energy window can be found for selective removal of the ITO films. The mechanical stress effect is apparently dominated the material cracking and delamination process. On the contrary, figure 6.1(b) shows cases induced by 10 ps laser pulse irradiation. Compared to long pulse ablation, much clearer ablation craters can be obtained with almost no heat affected darken area around the spots. With high fluence ablation, melting and fast re-solidification traces of ITO material can be observed. No cracking and delamination is observed for all laser fluences applied. The ITO film can be selectively removed by thermal evaporation with suitable pulse fluence.
6. Laser Ablation of ITO Film on PET Substrate

Figure 6.1: Ablation geometries of ITO films by 300 ms and 10 ps laser pulses. The fluences used are: (a). 0.06 J/cm², 0.09 J/cm², 0.25 J/cm² and 1.2 J/cm², the scale bar is 200 µm. (b). 0.61 J/cm², 0.89 J/cm², 2.8 J/cm² and 5.2 J/cm². The scale bar indicates 20 µm.

6.3.2 Substrate effect

The benefits of ITO film coated on glass substrate is that glass poses better compliant properties to the ITO material and strong adhesive strength to the film. With ultra-short pulse length irradiation, as discussed above it is possible to ablate the ITO film using a thermal evaporation process, giving qualified ablation patterns and rim performance. However, the challenge comes when applying laser to ablate ITO film coated on flexible substrate, due to the huge difference of thermal properties and relatively worse of adhesive strength. Although both glass and PET material are almost transparent to the 1064 nm wavelength pulse, different ablation mechanisms of ablation ITO film on both substrates can be found. Figure 6.2 shows the ablation morphologies by picosecond laser irradiation, where the film on PET substrate is seriously cracked. For high pulse fluence irradiation, solid phase delamination apparently dominate the ablation process. Figure 6.3(a) shows the ablation spot size as a function of applied laser fluence. The ITO film requires less pulse energy to initiate ablation on PET substrate.
6. Laser Ablation of ITO Film on PET Substrate

Figure 6.2: Ablation geometries of ITO film on glass and PET substrates by picosecond laser pulses. The fluences used are: (a) 0.61 \( J/cm^2 \), 0.89 \( J/cm^2 \), 2.8 \( J/cm^2 \) and 5.2 \( J/cm^2 \). (b) 0.78 \( J/cm^2 \), 0.80 \( J/cm^2 \), 0.90 \( J/cm^2 \), 1.0 \( J/cm^2 \) and 1.2 \( J/cm^2 \). The scale bar indicates 20 \( \mu m \).

<table>
<thead>
<tr>
<th>Unit: ( J/cm^2 )</th>
<th>ITO/Glass</th>
<th>ITO/PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064 nm</td>
<td>Threshold</td>
<td>Substrate damage</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>&gt; 8</td>
</tr>
</tbody>
</table>

Table 6.1: Critical thresholds in laser ablation of ITO film by pulses at 1064 nm wavelength with 10 ps duration.

In thermal evaporation dominated ablation processes like glass based films, a continuously increased trend of ablation depth is found. However, the depth remains almost constant until the PET substrate gets damage. The measured depth of the ablation spots indicates that the entire ITO layer was removed, as shown in figure 6.3(b). Table 6.1 lists some critical threshold fluences for determining the processing window. The easily damaged PET substrate narrows the processing window for selective removal of the ITO film.
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Figure 6.3: Ablation spot size and depth of ITO films on glass and PET substrate as function of pulse fluence.
6. Laser Ablation of ITO Film on PET Substrate

6.3.3 Wavelength effect

The wavelength effect has been discussed in reference [101], where the authors investigated the ablation of ITO film on glass substrates by 355 nm, 532 nm and 1064 nm with nanosecond pulse. Their results showed that only few difference in ablation geometries can be observed by different wavelengths. However, PET substrate has a high absorption of 355 nm and a relatively low melting temperature, ablation by pulses at 355 nm apparently demonstrates differences compared to ablation at 1064 nm wavelength. Figure 6.4 shows the ablation spots archived by picosecond pulse. At low fluence, symmetrical cracking channels are found starting from the irradiation center for both cases. For 355 nm, more cracking channels are observed. The film is delaminated and punched out from the substrate. For 1064 nm, the laser induced surface modification can be observed with the color change. At high fluence regime, the delaminated and curled ITO film around the spots was generated for both wavelengths, but was more serious for 355 nm. The curled film and the relatively smooth area of the exposed substrate indicate a delamination process. Figure 6.5 shows the ablated spot size and depth changes dependent on the applied laser fluence. Lower damage threshold for 355 nm wavelength pulse can be seen. Apparent damage to the PET substrates happens at the fluence above 1.8 J/cm² for 1064 nm wavelength and 3.1 J/cm² for 355 nm wavelength pulses. The processing window

![Figure 6.4: Ablation geometry with picosecond laser pulse by front-side irradiation. (a)(c) are induced by 355 nm pulses and (b)(d) are induced by 1064 nm pulses. The fluences used are: (a). 0.14 J/cm², (b). 0.56 J/cm², (c). 0.50 J/cm²; (d). 3.2 J/cm². The scale bar indicates 2 µm.](image)
6. Laser Ablation of ITO Film on PET Substrate

Figure 6.5: Ablated spot size and depth changes dependent on the applied laser fluence.

for 355 nm wavelength is larger in single pulse ablation. However, due to the high absorption of PET substrate at this wavelength, it narrows the processing window in case of multi-pulse overlapped patterning of lines or areas. The substrate damage location, for 355 nm was always located at the overlapped area. In contrast, for 1064 nm it was always located at the center of the spots, as shown in figure 6.6. For comparison, the same type of PET foil used for substrate in ITO coating was irradiated. In table 6.6 the different critical fluence thresholds
6. Laser Ablation of ITO Film on PET Substrate

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>ITO Damaged</th>
<th>ITO Removed</th>
<th>Substrate</th>
<th>PET foil</th>
</tr>
</thead>
<tbody>
<tr>
<td>355 nm</td>
<td>0.23</td>
<td>0.36</td>
<td>3.32</td>
<td>0.65</td>
</tr>
<tr>
<td>1064 nm</td>
<td>0.77</td>
<td>1.41</td>
<td>2.38</td>
<td>5.43</td>
</tr>
</tbody>
</table>

Table 6.2: Laser fluence thresholds for ITO damaged, removed and PET substrate damaged. For comparison, thresholds for laser ablation of pure PET material are also demonstrated. (Unit: \( J/cm^2 \))

are listed. From the table, we can deviate that the coated ITO layer protects the underlying PET from damage by using 355 \( nm \) wavelength pulses, but decreases the damage threshold by using 1064 \( nm \) wavelength pulses.

Figure 6.6: Ablation geometry with nanosecond laser pulse by front-side irradiation. The fluence used are: (a). 1.41 \( J/cm^2 \), (b). 1.84 \( J/cm^2 \).

6.3.4 Multi pulse effect

In practical application, laser scribing of isolated lines or areas is the result of multi-pulse ablation by setting a specific overlapping rate. In the last chapter we investigated the incubation effect of picosecond laser pulse ablation of ITO film on glass substrates at 1064 \( nm \) wavelength, where an incubation coefficient of \( S = 0.82 \) is determined by equation 5.2. Figure 6.7 shows the incubation effect for multi picosecond laser pulse irradiation onto the ITO film on glass and PET substrates. With glass substrates, the incubation coefficients deviated from the fitting lines, which demonstrate the same value for both wavelengths, where
6. Laser Ablation of ITO Film on PET Substrate

Figure 6.7: Incubation effect determined by threshold fluence as function of applied pulse number.

Figure 6.8: Cumulative effect in laser ablation of ITO film (a). by 1064 nm wavelength with 4 pulses, 7 pulses and 10 pulses. (b). by 355 nm wavelength with 1 pulse, 4 pulses and 7 pulses.
6. Laser Ablation of ITO Film on PET Substrate

\[ S = 0.82 \] can be determined. The ablation at both wavelengths is regarded to be a thermal evaporation process where a similar cumulative effect is found. An incubation coefficient of \( S = 0.85 \) is obtained by pulses at 1064 nm for PET substrates. The ablation by 355 nm pulses shows a very weak cumulative effect for PET substrate, where almost \( S = 1 \) is found. Figure 6.8 shows the multipulse ablation geometries of ITO film on PET substrate by 355 nm and 1064 nm wavelengths. For 1064 nm, the ablation spots get bigger by increasing the incident pulses, demonstrating a cumulative effect. However, for 355 nm pulses ablation, the subsequent pulse irradiation does not change the ablation geometry so much, although kind of surface modification can be observed.

6.3.5 Theoretical discussion

As observed, the thermal induced melting and evaporation or the stress induced cracking and delamination are the main ablation mechanisms involved in the removal of ITO film from glass or PET substrates. With better compatibility of thermal properties and better adhesive strength between glass and ITO films, the laser ablation of ITO films on this substrates are more likely based on the thermal melting and vaporization, but could be affected by the pulse width. Although the shorter pulse irradiation causes a higher amplitude of compressive stress, the restricts from either the surrounding film or the glass substrate constrains the film deformation which avoiding the mechanical failure of the film. As observed for picosecond and nanosecond laser ablation of ITO on glass, the removal mechanisms is attributed to the thermal evaporation. However, for long pulse irradiation, due to more heat energy is guided to the glass substrate, it causes the tensile stress in the film because of thermal expansion of glass substrate. Crack is initialized easily when the ITO film undergoes tensile loading [119]. Based on the equations 6.1-6.6 with the solution of FEM methods, we can parametrical study the stress change induced laser pulse irradiation in the film. Figure 6.9(a) shows the simulation results which record the history of the maximum radial stress \( \sigma_{rr} \) in the film.
6. Laser Ablation of ITO Film on PET Substrate

induced by 100 \textit{ns} and 0.1 \textit{ns} pulses irradiation. Upon initial exposure, the film expands quickly due to the temperature increasing, inducing a relatively highly compressive stress in the film, particularly when using short pulse where small heat diffusion length is fulfilled due to the confinement of the surroundings, either the film or the substrate. For long pulse, the heat conducting to the substrate causes the thermal expansion of the substrate, which could convert the compressive stress to tensile form if less thermal expansion of the film is found. It is observed that the initial compressive stress decreases quickly as the heat diffuses out of the irradiation volume. Figure 6.9(b) shows the maximum amplitude of compressive and tensile during irradiation with different pulse length irradiation. The results reveals that the substrate affects the stress distribution when it obtains enough heat energy from the film. The thermal penetration depth, which is mainly dependent on the pulse length, determines the amount of heat energy conducting to the substrate. From this point of view, the film thickness could also influence the amount of heat conducted to the substrate for a specific pulse length. Figure 6.10 demonstrates the simulation results. For thinner film, the stress amplitude for both compressive and tensile form is greater than the thicker ones. Therefore the film is more likely to be removed by mechanical stress. The experiments result in reference [120] confirmed that the stress delamination is the main reason for the removal of thinner ITO film from glass, rather than thermal evaporation for the thicker film.

In cases where the ITO films are on PET substrates, the laser induced mechanical stress plays a more important role in the ablation process. The high thermal expansion coefficient of PET material makes the upper film suffer tensile stress easily even at relatively low temperatures. As shown in figure 6.11, for PET substrate the compressive stress in the film upon the same pulse width irradiation converts to tensile form in a very short time. On the other hand, it has to be noted that the stress wave propagates as longitudinal and transverse acoustic waves. It will get reflection at the film and substrate interface due to the acoustic impedance mismatch with a reflection coefficient \( R_{\text{ac}} \), mentioned in equation 2.23.
6. Laser Ablation of ITO Film on PET Substrate

For ITO and glass contact, $R_{ac} = 0.523$ and for ITO and PET $R_{ac} = 0.997$. The high reflection coefficient, the stress wave at ITO and PET interface gets a significant energy deposition, enhances the delamination and converts to the kinetic energy of the fragments.

![Figure 6.9: The time history of the maximum stress inner the film induced by laser irradiation on ITO film. With different pulse length (a). The maximum compressive and tensile stress (b).](image-url)

Figure 6.9: The time history of the maximum stress inner the film induced by laser irradiation on ITO film. With different pulse length (a). The maximum compressive and tensile stress (b).
6. Laser Ablation of ITO Film on PET Substrate

On the other hand, the melting temperature of ITO material is about 2000 °C, but the PET material softens at about 70 °C and starts melting at about 200 °C, during the pulse irradiation, a very thin layer of PET in a depth of thermal diffusion length near the interface to the film is heated up, as schematically shown in figure 6.12. Before the ITO film reaches its melting temperature, such thin layers of PET undergo a phase of change, become glass transitions leading to a high volume expansion. This enhances the tensile stress amplitude of the ITO film. Moreover, the softened PET layer weakens the contacting strength to the film and loses the confinement of the film cracking and delamination. Therefore, compared to the ablation of ITO film on glass substrates, the film gets higher mechanical stress and less adhesive strength from the substrate, which leads to easy cracking and delamination, which usually occurs with low temperature under the film’s melting point. It is much worse for 355 nm pulse due to high absorption of PET material at this wavelength. As observed, more cracking channels were found in 355 nm pulse ablation. With high fluence irradiation, the heated volume of PET substrate near the interface could even be vaporized. The high volume expansion of the gas plume could punch out film and convert to kinetic energy of

![Figure 6.10: The time history of the maximum stress inner the film induced by laser irradiation on ITO film with different film thicknesses.](image)

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6. Laser Ablation of ITO Film on PET Substrate

Figure 6.11: The history of the maximum stress in the ITO films on glass and PET substrates under irradiation of nanosecond pulse.

Figure 6.12: Schematically demonstration of the softened layer of the PET substrate near the interface under the pulse irradiation on ITO film.
6. Laser Ablation of ITO Film on PET Substrate

the fragments. As one can see the serious curled area of the film at the perimeter of the ablation spots by 355 nm pulse ablation is much larger than that induced by 1064 nm pulses.

6.4 Picosecond Laser Ablation of ITO Film on PET

The experimental investigation demonstrates the pulses at 355 nm, 532 nm and 1064 nm are able to selectively remove the ITO film on PET substrate, as shown in figure 6.13. The 1064 nm pulse ablation exhibits a much smoother and clearer rim around the perimeter of the ablated spots than those by 532 nm and 355 nm pulses. The 532 nm and 355 nm pulse ablation results demonstrate a serious delamination effect, no matter what pulse energy above the ablation threshold is applied. The detached ITO thin film at the edge is curled from the central part. This makes it difficult to obtain clean and smooth edges of the ablation area with acceptable shoulder height for the industrial application without further beam shaping.

![Figure 6.13: Ablation spots induced by different wavelength pulses. (a). \( \lambda = 355 \text{ nm} \). (b). \( \lambda = 532 \text{ nm} \). (c). \( \lambda = 1064 \text{ nm} \).](image)

Similar to the single-pulse ablation, the ITO layer could easily be removed by 355 nm pulses with multi-pulse ablation of lines, but the edge of the lines are curled up. For 532 nm we face the same problem, it is difficult to get acceptable
6. Laser Ablation of ITO Film on PET Substrate

ablation edges, although the underlying PET substrate remained little affected in a relative large processing window of the laser energy. The typical geometries of the patterning lines are shown in figure 6.14. The best patterning results are obtained by 1064 nm pulse. For this reason we focus on the investigation of 1064 nm wavelength pulses. First the different laser irradiation direction, irradiation from front-side and rear-side of the ablated spot are illustrated in figure 6.15. The front-side ablation induces lots of curled strips at the edge of the ablated spot, leading to an unclear ablation spot. Pieces of fragments are observed in this case. The rear-side ablation demonstrates cleaner and sharper spots with little delaminated strips at the perimeter of the spots. Based on the results in the following analysis, rear-side irradiation is performed.

During the multi-pulse ablation, the overlapping rate and the laser fluence are the most important parameters and should synchronously optimize. The challenge always comes from how to decrease the shoulder height at the rim of the ablation area. The existing incubation behavior matters when patterning lines or areas, as discussed in the last chapter. Examples of patterned lines with different
overlapping rates are shown in figure 6.16 by optical microscopy. For lower overlapping rates, the edges of the ablation trench are much clearer and the substrate PET suffers less heat damage, but gives a higher risk of electrical interlinked path through the trench. As the overlapping rate increase, the ablation trench width and depth increase, which can be easily seen in figure 6.17. By increasing the overlapping rate, more and more small sharp sawtooth edges emerge. Visible damage of the PET substrate appears as the overlapping rates exceed 50%.

As discussed above, rear-side irradiation, fluence slightly above ablation threshold and relatively low overlapping rate could lead to superior quality of patterning results. By synchronously optimizing these parameters, clear selective patterning of the ITO layer could be achieved by 1064 nm pulse illustrated in figure 6.18. The laser fluence applied here is 0.89 J/cm² with an overlapping rate of 15%. For better observation, the sample has been tilted for pictures and the cross section profile is measured by stylus profile meter. From the SEM picture we can see that the edges of the patterned trenches are sharp and clean. No apparent damage of PET substrate is observed. The profile of the scribed trench revealed that the etching depth is approximately the same as the ITO layer thickness of 100 nm. Figure 6.19 shows another example of selective area removal of ITO layer conducted by 1064 nm laser pulses. The overlapping rate was set to 30% and the

Figure 6.15: Laser irradiation from front-side and rear-side directions for ablation with wavelength of 1064 nm.
Figure 6.16: Patterning line structure produced by different overlapping rates by 1064 nm wavelength pulses.
6. Laser Ablation of ITO Film on PET Substrate

laser fluence used was 0.89 $J/cm^2$. Figure 6.19(b) shows the cross section profile. The 100 $nm$ thick ITO layer was totally removed with only minimal damage to the PET substrate.

EDX analysis of the relative content of indium is carried out along the solid line shown in figure 6.20(a), located in the ITO removal area. For reference,

Figure 6.17: The width and depth of the ablation line varies by different overlapping rate.
Figure 6.18: (a). Line patterns by 1064 nm wavelength pulses with overlapping rate 15%. (b). Cross section profile of the patterned line measured by stylus profile meter.
6. Laser Ablation of ITO Film on PET Substrate

EDX characterization of native ITO coated PET was also detected, and this is shown as a dashed line. The results are plotted in Figure 6.20(b) respectively. The contrast in the contents of indium demonstrates the complete removal of the ITO layer and verifies the selective patterning ability of 1064 nm picosecond laser pulses. But it has to be mentioned that the ablation quality is very sensitive to the location of the sample referred to in the focus plane. Much difference can be observed by focus and defocus ablation.

Figure 6.19: (a). The patterning area induced by 1064 nm laser pulse. (b). The cross section profile obtained by stylus profile meter.
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Figure 6.20: EDX measurements of the relative content of indium in the ablated area (solid line) and the virgin ITO surface (dash line).
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6.5 Conclusion

In this chapter the selective laser ablation of ITO thin film coated on glass and PET substrate by picosecond laser is discussed. The parametric study reveals that the ablation of ITO film on glass substrate are more likely to be a thermal evaporation process. The mechanical stress induced cracking only found in ablation with long laser pulse length or with very thin ITO film. The ablation of ITO film on PET substrate are mainly induced by mechanical stress with cracking and delamination, especially for 355 nm wavelength pulses, due to the high absorption of PET material at this wavelength. Superior quality of the patterning lines and areas were obtained by synchronously optimizing the laser pulse fluence and pulse overlapping rate with rear-side irradiation strategy by pulses at 1064 nm wavelength.
Chapter 7
Conclusions and Prospect

7.1 Conclusions

Pulse laser ablation finds lots of applications in precise manufacturing in different industries. A thorough understanding of the underlying mechanisms of the laser-matter interactions and the subsequent laser-induced thermal effects are very critical for optimizing practical applications. For short pulse ablation, the capability to precisely control the laser energy coupling to target materials and precisely control the thermal diffusion loss to surroundings makes it suitable for laser micro structuring of solids. In laser ablation of bulk material, the laser energy coupling mechanisms and the thermal diffusion length are significantly influenced by the pulse length. Accurate control of the removal mass amount can be realized by shorter pulse ablation. An important finding in the laser ablation of bulk material is the dependence of the ablation threshold fluence on the applied pulse length, where linear dependency in short pulse regime is observed and independency for metals and nonlinear dependency for semiconductors in ultra-short pulse regime are found. Based on this conclusion, a characteristic pulse length can be defined which classifies the short and ultra-short pulse concepts in laser ablation. In this work, we focused on the pulse laser interaction with film-substrate system, aimed on selective laser ablation of thin films from based substrate. Short and ultra-short pulses ablation of widely used metal and
semiconductor ITO films have been discussed.

We have demonstrated that the pulse laser ablation threshold in film-substrate systems is significantly influenced by the optical penetration depth and the thermal diffusion length. A thermal penetration depth has been defined as the function of optical length and thermal diffusion length, which can be calculated by treating the laser as a surface heat source. However, due to the complicated nonlinear absorption of laser pulses for transparent semiconductors, for example for ITO films, theoretical prediction of thermal penetration depth is difficult. Experimental results on investigation of the threshold fluence dependent on the film thickness reveal the difference for metal and ITO films when the film thickness is in the range of thermal penetration depth. The single-shot ablation threshold was found to increase as the film got thinner, which is opposed to the behavior of metals. We identified the theoretical explanation for different variation regimes of the threshold fluence versus the film thickness for metal and ITO films. The influence of the thermal penetration depth on the ablation process has been illustrated by the different ablation characteristics observed by front- and rear-side irradiation for samples with different film thicknesses.

We have further studied the incubation effect existed in multi-pulse ablation. The variation trends of the ablation threshold fluences dependent on pulse number reveals the different cumulative mechanisms for metal and ITO films. We have especially demonstrated that when the film thickness is in the range of thermal penetration depth, the incubation behaves in a different way compared to the bulk samples. For ITO films, the incubation coefficient $S = 0.82$ was obtained by approximation and turned out to be independent of the film thickness, at least in the range of the film thickness between 10 nm and 100 nm. A simple mathematical model describing the influence of the incubation effect during laser patterning of ITO has been developed, which allows us to predict the width of patterning lines with varying overlapping rates between two succeeding pulses. The results can be transferred to the laser patterning of any material obeying an
incubation expressed by $F_{th}(N) = F_{th}(1)N^{S-1}$.

In addition, we investigated the influence of substrate on laser selective patterning of ITO film. We have demonstrated that the thermal evaporation and thermal induced mechanical stress can be the reasons for pulse laser ablation of ITO films on glass and PET substrates with parametric studies in both experiments and theoretical calculations. With parametric optimization, the possibility of picosecond laser selective ablation of ITO film on PET substrate has been illustrated.

### 7.2 Prospect

In this work we investigated the thermal penetration depth through experiments. Due to the complexity of interaction of the laser and semiconductors, there is still room for further investigation for the thermal penetration depth in theoretical aspect. For metals, the thermal penetration depth with ultra-short pulse irradiation is essentially governed by the hot electrons penetration depth. Based on theoretical analysis it is established that through the thermal penetration depth, the electron-phonon coupling strength can be well estimated. In case the metal thickness is thinner than the thermal penetration depth, the electron scattering in a vertical direction is limited by the boundary, for example the metal-dielectric interface, which could cause electrons or energy reflection. For thinner films the reflection energy should be more significant and will affect the electrons scattering in a lateral direction, especially for ultra-thin films. Detailed experimental and theoretical investigation can be done in these aspects. In ultra-short laser irradiation of semiconductor films like ITO material, the thermal penetration depth reflects the nonlinear interaction process of the electron-photons and electron-phonons. By constructing a suitable theory model, with the known thermal penetration depth obtained from the experimental method, it offers a feasible way to estimate the nonlinear absorption of the semiconductor materials.

There are still lots of debates about the mechanisms of the generation of
incubation effects in multi-pulse ablation. The former investigation are mainly focused on the mechanical frustration or the damage of electron bandgap. When the target is in film form, as we observed in our experiments the incubation behaves a different way as it in its bulk form both for metals and semiconductors. Further experiments such as pump-probe technology could be applied to investigate the kinetic process of the laser-induced material change, where more detailed evidence could be obtained to explain the mechanism of incubation effects.

Furthermore, the discussion could involve more extensive materials, such as dielectrics and polymers.
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