Early Stage Material Motion and Transient Optical Properties of Metals after Ultrashort Laser Pulse Irradiation

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Ultrashort pulsed lasers have gained widespread use in laser material processing applications, as they enable precise ablation due to their highly efficient energy deposition and low thermal damage. Recent investigations using double laser pulses for metal ablation with temporal spacing in the region of a few picoseconds (ps) have shown that the laser ablation efficiency decreases for the subsequent pulse in the laser pulse train, when the pulse separation is greater than approximately 5-10 ps. In order to understand this process the interaction between the ultrashort laser pulse and the metal must be understood. The early stage material motion and transient material properties can be analyzed using pump-probe ellipsometry, which allows the calculation of the transient complex refractive index in ultrashort timescales. By examining the transient change in the complex refractive index the ablation dynamics of four metals [Stainless Steel (AISI304), Aluminum (Al), Molybdenum (Mo) and Copper (Cu)] are investigated. All four metals show a strong decrease in the extinction coefficient *k* within a few picoseconds after irradiation, which is due a density decrease in the metal, generated from the high pressure induced by the femtosecond pulse. The results are discussed in terms of the impact for double pulse laser ablation of metals.
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1. Introduction

Material processing with ultrashort pulsed laser radiation with pulse durations in the picosecond and femtosecond range offers numerous advantages and more opportunities compared to nanosecond or microsecond laser pulses. Ultrashort pulse lasers allow material removal with increased precision and efficiency [1–3]. Processed structures have a minimal amount of thermal damage in the surrounding material due to the efficient deposition of energy in the target material. This has led to a wide range of applications which take advantage of the high quality processing capabilities of ultrashort laser pulses, including applications such as selective thin film structuring [4–6], ablation of dielectrics [7,8] and metal processing [9,10]. When an ultrafast laser pulse interacts with a metal target, a number of transient processes take place in the material. A good description of the material dynamics can be obtained by applying the two temperature model, which describes the thermal coupling between the electron and lattice subsystem of the material [11]. Firstly the energy is absorbed by the conduction band electrons in the material, this is followed by thermalization of the hot electron gas by energy transfer to the lattice, typically taking place on a picosecond timescale. As the lattice heats up pressure builds up in the absorption region, followed by phase change if the temperature increase is sufficient. Material removal can be induced via a number of processes such as melt spallation [12], phase explosion [13], and vaporization [14]. The ablation characteristics and transient dynamics may be influenced by a number of laser parameters such as the applied fluence [15], the laser pulse duration [16], and the number of incident laser pulses [17]. Often for multiple incident laser pulses the subsequent laser pulses may interact with a material surface which has an altered reflectivity [18] or an increased number of defects for absorption [19].

For an in-depth understanding of the laser material interaction, knowledge of how the material properties react on an ultrashort time scale is necessary. This can be achieved by using advanced experimental techniques such as time-resolved pump-probe ellipsometry, which allows the measurement of the transient change in the complex refractive index. The complex refractive index is given as $N = n\text{-}ik$, The information about the transient density of the metal is included in the extinction coefficient k of the complex refractive index which can also be converted into the optical penetration depth d and absorption coefficient of the material [20].

Pump-probe ellipsometry has been applied to study the transient optical properties of numerous materials including

copper [20], gold thin films [21], and molybdenum [22]. The experimental results can be used to obtain deeper understanding of scientific and industrial relevant material ablation properties, including ablation efficiency of metals [23], processing with pulse bursts [24], and high repetition rate material processing [25]. Recent investigations of metal machining have primarily used IR wavelength pulses, where laser sources can generate very high powers for high throughput machining [26]. The use of double pulses for metal ablation has been studied, where subsequent pulses are separated on the order of a few picoseconds to hundreds of picoseconds. The pulse separation time has a large impact on the overall ablation depth and therefore the ablation efficiency of the process. Pulse separations from 0.2 to 1 ps result in a large increase in the ablation depth compared to a single incident pulse, while for pulse separations from 5-100 ps the ablation depth for double pulses is less than that for a single pulse. This behavior has been noted for a range of materials including Cu [27], Al [28] and Ni [29]. The mechanics of the process has been studied using hydrodynamic models, which have hypothesized that the reduction in ablation depth is due to the suppression of the generated rarefaction wave by the second incident pulse [28].

In this study the transient change in the extinction coefficient k is analyzed in the timescale up to 50 ps after laser irradiation for four industrially relevant metals. The change in the extinction coefficient k is used to show how the transient early stage change in material properties affects the processing of industrial relevant materials, in this case irradiation of metals using double pulses.

2. Experimental methods and materials

2.1 Ellipsometry experimental setup

Pump probe ellipsometry was used in this work to analyze the change in the complex refractive index of the four metals. The experimental setup is shown in Fig. 1. The laser source for the pump probe setup is a Nd:Glass laser (Spectra Physics, "femtoRegen") delivering pump pulses at a center wavelength of λ_{pump} = 1056 nm and a pulse duration of τ_{pump} = 680 fs (FWHM). The beam is then split into pump and probe branches, with the probe branch frequency doubled in a second harmonic generation module, in order to filter out the pump pulse from the imaging module. This results in probe pulses with a center wavelength of λ_{probe} = 528 nm and a pulse duration of τ_{probe} = 540 fs. The optical delay line allows the probe pulse to be delayed up to 1 ns after delay time zero, with a temporal resolution of approximately 1 ps. In this study the optical delay line is used to delay the probe pulse to sample the material response up to 50 ps after the initial incident pump pulse to observe the early optical material response which is most relevant to this study. A full detailed description of the measurement procedure and the data post processing method is given in [22].

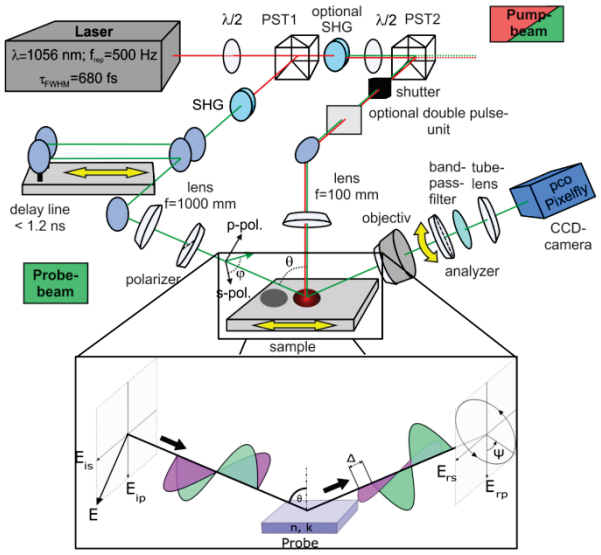

Fig. 1 Pump probe ellipsometry setup for the determination of the transient change in complex refractive index for each metal target. The box at the bottom illustrates the change in polarization after reflection from the metal surface

2.2 Materials

In this work four metals were studied including AISI304, Al, Mo and Cu. For AISI304, Al and Cu the material had a thickness of 500 µm, whereas Mo had a thickness of 430 µm. Each metal target can therefore be classified as bulk materials because the absorption depth is much smaller than the sample thickness for the wavelengths used in this study. To guarantee a homogeneous sample surface – which is crucial for ellipsometry measurements, the samples were carefully polished using a two-step mechanical polishing procedure. Firstly a grind polish consisting of decreasing grain sizes from 10 – 6 µm is performed on the metals, followed by a polish with decreasing grain sizes from 6 – 0.02 µm. This results in a metal surface with an average surface finish of R_a < 25 nm.

2.3 Threshold fluence determination

In order to give an accurate comparison point, for each metal the threshold fluence F_{th} for laser ablation was determined using the D^2 method (or zero-damage method) [30]. The ablation threshold fluence is defined as the minimum incident energy density which is required for a visible surface modification on the material observed usually by optical microscope or SEM, and is typically given in units of J/cm^2.

3. Results

Firstly the threshold fluence was determined for each metal target, giving values of 0.29, 0.87, 0.54 and 2.2 J/cm^2 for AISI304, Al, Mo and Cu respectively. These threshold fluences are used as the relative point for the comparison between each metal, in order to ensure uniform irradiation conditions. In order to examine the effects of the ablation process on the transient material properties, the fluence for the pump-probe ellipsometry experiments was set to 1.3 × F_{th} for each respective metal. From this extinction coefficient was determined from -15 ps to 50 ps after the irradiation, as shown in Fig. 2.

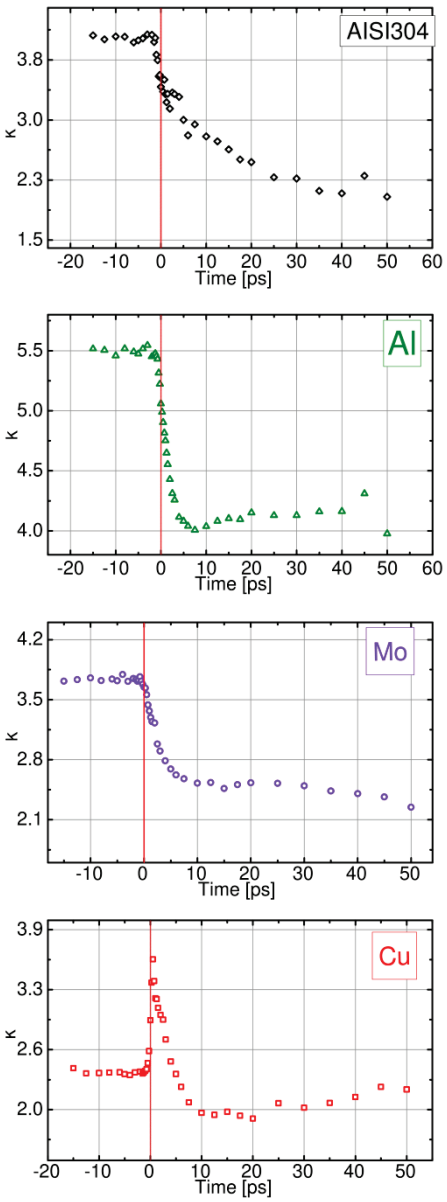

Fig. 2 Change in the extinction coefficient *k* for the four metal targets AISI304, Al, Mo and Cu at probe time steps from -15 to 50 ps

For each metal the initial *k* value before ablation occurs was determined to be 4.11, 5.45, 3.73 and 2.37 for AISI304, Al, Mo and Cu, respectively. These steady state values agree within a few % with values in the literature, which are given as 3.85 [31], 6.36 [32], 3.72 [33] and 2.60 [34]. The actual values of the complex refractive index depend on the wavelength of the probe radiation used in the literature, and also on aspects such as the fabrication conditions, sample preparation or thin oxide layers, which explains the small variations in the experimental values seen here and those in the literature.

As the pump laser irradiates the metal target the values of *k* undergo a rapid change, with various trends noted for each metal. Firstly for AISI304 the *k* values decrease immediately as the pump pulse irradiates the surface. The fall off time can be defined as the reduction in k from 90 % to 10 % of the amplitude change from maximum to minimum values, as typically used in signal analysis The maximum is taken as the average steady state value in the negative probe delay time, and the minimum is the local minimum in the first rapid drop in values. For AISI304 the fall off can be spilt into two regions. The first fast fall off occurs up to 2 ps, with a decrease of 4.11 → 3.15. The second decrease occurs over a much longer time scale from 2 to 50 ps, with a final minimum value of 1.93. For Al and Mo the general trend for the *k* values is roughly similar, with a reduction in both *k* values of 5.45 → 3.97 and 3.71 → 2.24 respectively. The fall off times for both metals are in the same time regime observed for AISI304, with times of 4.5 and 5 ps respectively. In the case of Cu the dynamics of the transient changes in *k* are different in the early time stages. As the laser pulse irradiates the Cu sample, the values of *k* undergo a rapid increase peaking at 3.6 at a delay time of approximately 500 fs. This increase in *k* values is due to the excitation of d-band electrons[20]. A rise in the electron temperature evolution up to several thousand K induces a broadening of the Fermi-Dirac distribution around Fermi energy and leads to a redistribution of occupied electrons. A reduction in electronic occupation number below the Fermi energy causes an enhancement of the linear absorption for photon energies smaller than the interband transition threshold (ITT), whereby for photon energies higher than ITT (ITT = 2.15 eV for Cu, with a probe pulse at 2.35 eV [35]) a strong reflectivity increase was experimentally and theoretically studied [37]. This redistribution process at Fermi energy will strongly affect the optical response of the probe pulse. The experimental evidence of this behavior in the linear optical response was provided by Hohlfeld et al. and explains the wavelength dependence in the pump-probe measurements on the metals by taking into account only the variation of the dielectric function at electron temperatures up to 4000 K [37].

In the case of Cu, the excitation process of energetic low-laying d-band electrons takes place already after reaching electron temperature of ~5000K [20]. Finally, probing of electrons with photon energy higher than the ITT into an already thermally occupied d-band electrons, results in a higher electronic concentration in the conduction band and thus a steep increase in plasma frequency of the quasi free electron gas. This induces a rise of the extinction coefficient *k*. The thermal excitation is dominant especially at higher temperatures and in following at higher fluencies at or above the threshold fluencies, where the temperature of several ten thousand kelvin can be reached.

After this initial increase the *k* values have a fall of time of 7.5 ps to a local minimum, with a decrease of 2.4 → 1.85. For all of the four metals tested, the general trend in the first 50 ps after irradiation is the same, with a large decrease in the observed *k* values. The initial quick *k* fall off for all four metals occurs in the first few ps after irradiation, and can be in general related to the electron-phonon coupling time, which describes how quickly the electrons couple the absorbed energy to the lattice [20]. Typical electron phonon coupling times are estimated in ps for AISI304, Al, Mo and Cu as 1 [38], 2 [39], 3.5 [40] and 10 [20].

In the case of ultrashort laser pulse irradiation, the energy is deposited first to the electronic subsystem and then transferred to the lattice on a much longer picosecond time scale. For ultrashort pulse irradiation a critical parameter is the stress confinement time, which is defined as $\tau_s \sim L_p/C_s$, where L_p is the energy penetration depth and C_s is the speed of sound in the material [41]. For the pulse durations and metals used in this study the condition for stress confinement is met, with theoretical stress confinement times in the region of a few ps for metals. This results in a high compressive stress generated in the absorption region after the pulse is absorbed, as the pulse duration is shorter than the acoustic relaxation time. The high thermoelastic pressure results in surface expansion of the material which causes an unloading of the stress into the material. This compressive stress generates two waves in the material, a pressure wave which propagates into the material bulk, and another which propagates to the material surface. The wave is then reflected back from the surface into the material as a rarefaction wave. This results in a decrease in the material density ρ in the surface region, evolving on a picosecond timescale, seen in Fig. 2. as a decrease in the k values for all metals. The extinction coefficient is directly related to the material density in terms of the atomic concentration, and can be fully formulated using the Drude critical point model [42]. Typical pressures generated in Cu for femtosecond pulses can be in the region of 35 GPa, which can generate a surface expansion velocity of 650 m/s, 5 ps after the initial pulse absorption [20]. Here the simulated density decreases rapidly in the metal skin depth in the first few picoseconds after the pulse is absorbed, with an increase in density propagating into the material bulk. As the probe pulse used in this study is at 528 nm, the change in density is only observed in the skin depth, and as such only interacts with the portion of the metal which is decreasing in density. The role of early stage material phase change may also play a role in the decrease in density in the first 50 ps. In this study applied fluences are considered just above the threshold fluence, which would indicate potential for early stage melting in the skin depth. As such the change in density in this study is the sum of both the change in density due to the unloading of stress in the surface region and any melting which may occur. Other effects such as spallation, phase explosion, or in other terms nanoparticle ejection, plasma formation and ablation will occur on longer time stages than used in this study.

As discussed earlier, the efficiency of double pulses decreases significantly for the second pulse, when the pulse spacing is above a few picoseconds. This has been attributed to different effects such as reheating of the ablation plume [27], and suppression of ablation due to the interaction of the second pulse and propagating rarefaction wave, which is generated on a picosecond timescale [28]. The study presented here shows experimentally that the values of the k reduce for all of the metals due to a fast decrease in the material density at early delay times, driven by the pressure waves generated in the material. Our experimental analysis of the surface density decrease agrees the previous hydrodynamic simulations[28], where the pressure evolution in Cu after femtosecond laser pulse irradiation was studied. If a second pulse is incident during the rarefaction wave timescales, it will reduce the intensity of the wave, resulting in an overall decrease in the laser ablation depth and efficiency. The experimental decrease in k values can also be compared to double pulse experimental studies on Cu, where the crater depth was measured for both single pulses and double pulses with a varying temporal pulse spacing between 0.2 and 100 ps [27]. In this study the ablation depth between single and double pulses was much larger for double pulses if the pulse separation was below 2 ps. When the pulse separation reached 10 ps the ablation depths between the single and double pulses reaches parity. This agrees with our experimental results, where the fall off in the extinction coefficient k values occurs approximately 7-10 ps after the initial irradiation.

4. Conclusions

In this study the transient optical properties of four metals were examined in the first 50 ps after laser irradiation using pump probe ellipsometry. The results show that using femtosecond laser pulses results in a rapid decrease of the extinction coefficient k values in the first 50 ps after irradiation. This is due to a decrease in density in the absorption region, which results from compressive pressure waves generated by the unloading of stress in the absorption region. The inter pulse delay spacing of double pulses has a large impact on the interaction between the second pulse and the material. For delay times less than the stress confinement time the second pulse will be absorbed normally in the material surface, generating a high ablation efficiency. However when the delay time is greater than the stress confinement time, the second laser pulse reduces the intensity of the rarefaction wave, resulting in a decrease in the subsequent ablation depth and hence the ablation efficiency.

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