Double pulse ultrafast laser ablation of nickel in vacuum

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We have studied ultrafast laser ablation of nickel using a pair of identical ≈ 250 fs 527 nm laser pulses separated by ≈ 1 to ≈ 1000 ps. Scanning white light interferometry was used to measure the ablated volume, and an ion probe was used to measure the angular distribution of the ablation plasma plume and the total ion emission. As the delay of the second pulse increased from ≈ 10 to 100 ps the ablated volume decreased by more than a factor of 2; indeed it falls to a value below the single pulse case. Conversely, it is found that the ion yield is sharply increased in this delay regime. It seems that both these features can be explained by the interaction of the second laser pulse with the ablated material produced by the first pulse. © 2009 American Institute of Physics.

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I. INTRODUCTION

The study of ultrafast laser ablation (ULA) using a pair of pulses with controlled separation is receiving increasing attention due to the interesting synergetic effects, which arise both in the properties of the laser produced plasma (LPP) and in the morphological features of the ablation craters.^{1–4} Double pulse (DP) irradiation has been also used in experiments aiming to elucidate the ablation mechanisms, or to modify the properties of the ablated species.^{5,6} Most of these studies deal with ULA of a silicon (Si) target, while DP ULA of metals has been less investigated. Different features of the ULA process, such as ion yield, plasma emission intensity, or ablation depth, can be used to investigate how DP irradiation affects the plasma plume and the efficiency of the ULA process. Depending on the time delay between the pulses, the second pulse may interact with a modified target surface or with the ablated material produced by the first pulse. Since different physical processes, such as electron-lattice relaxation and hydrodynamic expansion, occur on different time scales, the time delay between the pulses can influence the final properties of the ULA products.

Several experimental studies of DP ULA of Si have been carried out. For example, Spyridaki *et al.*² used time-of-flight (TOF) mass spectrometry to study the increase in the number of ions measured for DP ablation of Si. They also noted that DP ablation yields a much smoother ablation crater. This was attributed to efficient energy coupling of the second pulse to the melted layer produced by the first acting to prevent the ripple formation, which occurred for single pulse (SP) ablation. Using emission spectroscopy, Hu *et al.*³ observed that a second delayed pulse causes an increase in the ion emission from Si. Again it was suggested that this increase was due to enhanced absorption of the second pulse at the molten surface produced by the first. Scuderi *et al.*⁵ studied DP ablation

of titanium and looked at the effect of delay on the nanoparticle production by making time resolved measurements of nanoparticle plume emission. They observed a considerable drop in this emission signal at delays ≈ 1 ns, which was attributed to interaction of the second pulse with the nanoparticulate matter leaving the target after the plasma component has expanded sufficiently to be optically thin to the second pulse. Semerok and Dutouquet⁷ studied DP ablation for short delays and for a range of laser pulse durations. They found that the ablation depth was effectively doubled with the addition of a second delayed pulse for delays < 1 ps. For longer delays the ablation depth decreased, until at 100 ps the depth was comparable to, if not slightly smaller than that observed for SP. In the range 0.1–2 ps, this behavior did not depend on the laser pulse duration, nor did the ablation efficiency. Plasma shielding was suggested as the cause. Noel and Hermann⁸ measured the spatially resolved atomic/ionic and nanoparticle emission from a DP ablation plume as a function of delay. With increasing delay, beyond the electron-lattice thermalization time, the plasma emission species increases while the nanoparticle emission decreases. Recently Amoruso *et al.*⁹ studied the role of laser polarization during DP ablation of aluminum and copper and found that more efficient ion generation occurs for *p* polarization, which was attributed to resonance absorption of the second pulse in the material ablated by the first. These various studies have enabled some understanding of DP laser ablation, although most of the experiments examine one specific feature of the DP process, such as ablated depth or ablation plume dynamics. It seems that an experiment that examines the behavior of several features may be useful.

In this paper we report the results of a study of DP ULA of a nickel (Ni) target in high vacuum, where we have measured the ablation plume characteristics (ion flux and angular distribution), and target ablation depth. A pair of identical laser pulses separated by a delay, $\Delta t \approx 1$ to several hundred picoseconds, was used. Our measurements indicate that the

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FIG. 1. (Color online) (a) Crater profile measured with ZYGO interferometer of an ablation crater produced by DPs separated by 200 ps delay. (b) Depth profile along the major axis of the crater.

second pulse can strongly modify the nascent ablation plume formed by the first pulse, and in turn influence the overall ULA process.

II. EXPERIMENT

ULA of Ni was carried out using ≈ 250 fs laser pulses at 527 nm. These pulses were formed by pulse compression and harmonic conversion of ≈ 1 ps pulses at 1054 nm from a Nd:glass laser. DPs were obtained using a Michelson interferometer. Both pulses were collinearly focused to an elliptical spot on a Ni target in high vacuum (10^{-7} mbar) with p -polarization and 45° incident angle. The pulse compression, harmonic conversion, and Michelson interferometer all have an influence on the final beam intensity profile, which is no longer Gaussian, as is evident from the ablation crater profiles. The energy of each pulse was ≈ 85 μ J and the ablation spot area was $\approx 6 \times 10^{-4}$ cm². The plasma part of the ablation plume was characterized using a planar negatively biased Langmuir probe¹⁰ oriented to face the target spot and located at a distance of 33 mm from the target. The probe collecting area was a 2.5×5 mm² copper plate insulated at the rear side. The angular distribution of the ion flux in the LPP was measured by moving the probe on a circle centered at the ablation spot. The target was rotated in its own plane to avoid drilling a hole. The ablation depth per pulse was found by irradiation of a stationary target with a fixed number of pulses (≈ 3000), and measuring the ablation crater with a ZYGO white-light three-dimensional surface profiler.

III. RESULTS AND ANALYSIS

Figure 1(a) shows an example of the depth distribution map, as measured with a ZYGO interferometer, for an ablation crater formed by DPs separated by 200 ps. Figure 1(b) shows the depth profile along the major radius of the elliptical crater. Crater depth profiles were measured for a range of delays and these are shown in Fig. 2. The depth profile for a SP irradiation is also shown. Using the data obtained from the surface profile measurements the total ablated volume and maximum ablated depth could be found for a given pulse delay Δt . These data are presented in Fig. 3. From Figs. 1–3 it is obvious that there is a clear dependence of the amount of

FIG. 2. (Color online) Depth profiles for ablation using DPs with various delays. The SP profile is also shown.

ablated material on Δt . For short delays the ablation volume and depth are more than twice the SP values. As Δt is increased beyond ≈ 10 ps the volume and depth are progressively reduced, falling somewhat less than the SP value for $\Delta t \geq 100$ ps. As shown in Fig. 2, this reduction in ablated volume is coincident with a dramatic change in the shape of the ablation crater: from a shape which reflects the beam intensity profile at short delay to a shallower flat-bottomed crater at long delays. Thus the action of the second pulse is to preferentially suppress ablation in the higher fluence regions of the beam spot.

The influence of a second delayed pulse on the expansion dynamics of the ionized ablated material was investigated using the Langmuir probe to record the ion TOF signals at different angles, θ , away from the target normal and for different delays of the second pulse. Figure 4 shows the ion signals along the target normal ($\theta = 0^\circ$) for different delays. The ion signal for SP ablation is also shown. For all values of delay the addition of the second pulse leads to a large increase in the amplitude of the ion signal. Both the amplitude and, to a lesser extent, the TOF at the peak are dependent on the delay. The average ion energy was calculated from the TOF signals in Fig. 4. For SP the average energy is 22.5 eV. For DP at small delays the average energy rises to 35 eV. It decreases as the delay is increased, such that at $\Delta t = 500$ ps it is about equal to the SP value, even though the amplitude of the ion signal is still several times larger

FIG. 3. (Color online) Ablated volume and maximum ablation depth as a function of delay between pulses. SP values are shown by arrows.

FIG. 4. (Color online) Ion TOF signals for different delays between the two laser pulses. SP indicates the signal for SP irradiation.

than for SP ablation. The ion signals in Fig. 4 were integrated to see how the ion yield in the normal direction depends on delay. This is plotted in Fig. 5, which includes additional data points corresponding to signals not shown in Fig. 4. The arrow indicates the ion yield for SP. At short delays ($1 \text{ ps} < \Delta t < 10 \text{ ps}$) the DP ion yield is almost constant, it starts to increase at $\approx 10 \text{ ps}$, reaches a maximum at $\approx 100 \text{ ps}$, and then falls at longer delays, eventually to below the short delay case for delays $> 300 \text{ ps}$. This behavior is very similar to that previously reported for DP ablation of copper and aluminum.⁹ Looking at the ablation depth (Fig. 3) and ion yield data (Fig. 5) together, it can be seen that the range of delay ($10 \text{ ps} < \Delta t < 100 \text{ ps}$) over which the ablation depth is reduced is closely correlated with the enhanced ion yield.

To see if the second pulse has any influence on the shape of the ion plume, we measured the angular distribution of the ion yield for a range of delays. For example, Fig. 6(a) shows the angular distributions of ion yield for SP and for DP at $\Delta t = 50 \text{ ps}$. For clarity the distributions have been normalized to the same maximum value. In both cases the distributions are strongly peaked in forward direction ($\theta = 0^\circ$), and the DP distribution is somewhat narrower. The distributions have been fitted with the angular distribution $N(\theta)$ predicted by Anisimov's model of ablation plume expansion for the case of deposition per unit area on a hemispherical surface centered on the ablation spot,^{11,12}

FIG. 5. (Color online) Ion yield at $\theta = 0^\circ$ as a function of the delay between pulses. The dashed curve is a guide to the eye. The arrow indicates the yield for the first pulse only (SP).

FIG. 6. (Color online) (a) Angular distribution of the ion yield with respect to the target normal for a SP and DP ($\Delta t = 50 \text{ ps}$) irradiations. The distributions have been normalized to the same maximum. The curves show the fit to Eq. (1). (b) k -value of the angular distribution as a function of the delay, Δt , between the pulses. The line is a guide to the eye. The arrow indicates the k -value for the first pulse only (SP).

$$N(\theta) = (1 + \tan^2 \theta)^{3/2} (1 + k^2 \tan^2 \theta)^{-3/2}. \quad (1)$$

From Fig. 6(a) it can be seen that this expression provides a good description of the shape of the LPP expansion for both SP and DP irradiation. The fitting parameter k in Eq. (1) is the asymptotic aspect ratio of the semi-ellipsoidal ablation plume in the plane of measurement, and is equal to the ratio of the plume radii normal to and parallel to the target surface in the inertial phase of expansion. A larger k corresponds to a more forward peaked expansion. The variation of k with Δt for DP irradiation is plotted in Fig. 6(b); the SP value is also shown. For DP irradiation at short delays k is higher than for SP. It increases further as the delay is extended to $\approx 10 \text{ ps}$, and finally falls back to the SP value at $\approx 500 \text{ ps}$.

IV. DISCUSSION

Our experimental observations point to a rather complex interplay between the different mechanisms involved in DP ULA as well as their influence on the overall relaxation dynamics of the excited target material and the final ablation depth. In DP ULA the nature of the optical interaction of the second pulse will depend on how the near-surface region of the target has evolved since the delivery of the first pulse, and thus on the delay Δt between the pulses. Molecular dynamics simulations and hydrodynamic modeling have shown that ULA is characterized by complex decomposition mechanisms.^{13–16} The laser heating is isochoric, and the subsequent relaxation dynamics leads to a complete atomization of a surface layer and a decomposition into a mixture of vapor and clusters through mechanical fragmentation and phase explosion of the rest of the ablated material. This leads to the appearance of two distinct ablation plumes in the far

field: a faster-moving atomic plume and a slower-moving nanoparticle plume, as observed in experiments.^{16,17} Typically, the atomic plume accounts for only 10%–20% of the total ablated mass.^{9,14,16} The SP fluence used here is higher than the ablation threshold fluence of Ni,¹⁶ and produces significant ablation (see Fig. 3) and plasma emission (see Fig. 4). The thickness of the surface layer relaxing into the atomic plume is estimated to be ≈ 2 –3 nm.

While a clear picture of ULA is emerging for the case of SP ablation,^{9,13–18} modeling of the DP ablation has not been done. However, it is possible to discuss our observations within the framework of current knowledge of ULA and related laser-matter interaction mechanisms. In particular, we discuss our results by taking into account the structure of the nascent plume after the first laser pulse: this is formed by a cloud of atomic particles extending far above the original target surface and a successive layer composed by a mixture of vapor and nanoclusters, which is closer to the original target surface.^{15,16} These two clouds give rise to the two plume components, i.e., the fast atomic plume, and the much slower (≈ 100 times) nanoparticles component, at long time after the laser pulse in the far field.^{16,17}

For Ni the characteristic time of electron-lattice energy transfer is ≈ 5 ps,¹⁸ therefore, for delays less than this time the second pulse interacts with an electron distribution, which is not in equilibrium with the lattice. This can explain the observed constancy of the ion yield and ablation depth for $\Delta t < 10$ ps (see Figs. 3 and 5). Moreover, while the DP ion yield increases almost sevenfold with respect to SP value, for $\Delta t < 10$ ps, the ablation depth is only doubled. For $\Delta t > 10$ ps, the second pulse interacts with the cloud of atomic particles, which finally forms the atomic plume at longer distance and time. This material expands at a velocity $u \approx \text{few} \times 10^5$ cm/s.^{15,16} The average density of this atomic vapor, resulting from ablation of an initial surface layer of thickness $d_0 \approx 2$ –3 nm, can be estimated as $n \approx (n_s d_0)/(u \tau)$, $n_s = 9.1 \times 10^{22}$ cm⁻³ being the solid Ni atomic number density. At delays of 10–100 ps, the second pulse strongly interacts with the atomic vapor, characterized by a density $n \approx (0.5\text{--}5) \times 10^{21}$ cm⁻³ and a temperature $T \approx (0.5\text{--}1)T_c$, where $T_c = (9470 \pm 40)$ K is the critical temperature of Ni.¹⁵ Under these conditions the high density, partially ionized atomic vapor can significantly absorb the second pulse through bound-bound and bound-free transitions as well as inverse bremsstrahlung. For *p*-polarized laser irradiation the absorption can also be further augmented by resonance absorption.^{9,19} At high density, the bound-bound transitions will be strongly Stark broadened and will overlap to yield quasicontinuous absorption, which can be much stronger than other mechanisms. This point is often overlooked in dealing with the emission and absorption properties of low temperature LPP. We have calculated the total absorption cross section using the spectral synthesis code PRISMSPECT,²⁰ which models the plasma ionization, level populations, line broadening, and spectral emission and absorption for a given temperature and density. For example for Ni with an atom density of 1×10^{21} cm⁻³, and a temperature of 0.8 eV, which is close to the critical temperature, the optical absorption cross section at 527 nm (2.35 eV) is calculated to be 2.3

$\times 10^{-18}$ cm². At these conditions the fraction of singly ionized Ni is only 2%. The average fluence in each beam is 0.14 J cm⁻², which corresponds to 3.7×10^{17} photons cm⁻². The probability that each atom absorbs a photon from the second beam is ≈ 0.9 , which corresponds to ≈ 2 eV per atom. This will produce a temperature rise of about 0.5 eV, which according to PRISMSPECT, will raise the fraction of Ni⁺ to $\approx 20\%$, thus explaining the dramatic increase in ion yield caused by the second delayed laser pulse. As the delay increases beyond a value around 100 ps, both the density and temperature of the atomic vapor component produced by the first pulse will decrease, the absorption cross section at the laser wavelength will decline rapidly, and the atomic vapor layer will become almost transparent to the second laser pulse. This is reflected in the ion yield measurements where for delays longer than 100 ps the yield starts falling rapidly.

It is now clear that the delay dependence of the ablation depth in Fig. 3 is strongly correlated with the shielding effect of the atomic vapor produced by the first pulse. In the regime where the ionization of atomic vapor is enhanced (≈ 10 –100 ps), and the second laser pulse is efficiently absorbed, the ablation depth falls significantly (see Figs. 3 and 5). However, at long delays ($\Delta t > 100$ ps), although the absorption of the nascent atomic vapor is gradually reduced, the second pulse can still be absorbed and scattered at the front of the following mixed vapor/cluster layer, and the ablation depth remains low, indeed at a value below the SP case.

Our findings seem to indicate that heating of either the nascent atomic vapor, or the deeper mixed vapor/cluster layer, modifies the successive relaxation dynamics of the irradiated material, finally reducing the ablation efficiency and, consequently, the ablation depth. While this feature requires further investigation, it seems that our observation may be similar to the reduction in the ablation efficiency recently reported for low-fluence ULA of a target wetted by a thin liquid film, which was studied using molecular-dynamics simulations.²¹ There it is shown that when the thin liquid film is suddenly heated to high temperature it relaxes along a supercritical trajectory to form a hot fluid layer above the surface of the heated target. The presence of such a high-pressure fluid layer significantly modifies the subsequent ablation dynamics such that deeper sections of heated target tend to relax back toward their initial solid state. This reduces the efficiency of material ejection and, in turn, the ablation yield. Thus it seems that in DP ULA when the second pulse is delayed by more than ≈ 10 ps, the rise in pressure caused by interaction of the second pulse with the nascent plume acts as a tamper, which impedes the decomposition of material deeper in the target and lowers the ablation depth. It thus seems that in ULA the use of DPs with a separation of more than ≈ 100 ps may be a way of obtaining more uniform craters.

Finally, we can also understand the observed change of the shape of the ion plume in the context of interaction of the second pulse in the nascent plume. First, it seems that the higher *k* value observed for DP with short delay, as compared to SP, is due to the formation of plasma over somewhat larger area when the net fluence is higher.¹¹ For delays up to ≈ 100 ps efficient laser absorption of the second pulse in the

nascent atomic vapor will lead to a larger area of plasma formation than for SP. For long delays we expect a gradual reduction of the absorption of the second laser pulse in the atomic vapor and k should progressively return to the SP value, which it does.

V. CONCLUSION

This investigation of DP ULA of Ni has shown that the addition of a second delayed pulse has a strong influence on the dynamics of the ablated material and the overall ablation process. This is ascribed to the interaction of the second laser pulse with the structured nascent plume formed by the first pulse. In particular, our experimental observations indicate a rather complex interplay between various mechanisms involved into the interaction of the second delayed laser pulse with either the atomic vapor or the mixed vapor/cluster layer forming the ablation plume produced by the first pulse, depending on the pulse separation. For delay of 10–100 ps the absorption of the second pulse in the atomic vapor produced by the first pulse leads to a progressive enhancement of its ionization. Moreover, as the delay of the second pulse is increased from 10 to 100 ps, the ablation depth and the ablated volume decrease sharply to below the SP values. For longer delays (>100 ps) the density, temperature, and optical absorption of the nascent atomic vapor decay and the ion yield is reduced accordingly. In this regime, the interaction of the second pulse with the mixed vapor/cluster layer keeps the ablation depth to low values, even below the SP case. It seems that absorption of the second pulse in the nascent plume acts to shield the target, and the pressure pulse created by the heating effect of the second pulse acts as a tamper that inhibits the subsequent decomposition of target material and reduces the overall ablation efficiency. Finally, our experimental observations suggest DP ablation as an interesting method for manipulating the characteristics of the ablation plume and crater shape, and indicate the need for a detailed modeling of the ablation induced by more complex laser

excitation schemes and of mechanisms influencing absorption, ionization, and hydrodynamics of the ablated material.

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