Enhanced absorptance of gold following multipulse femtosecond laser ablation

A. Y. Vorobyev and Chunlei Guo

The Institute of Optics, University of Rochester, Rochester, New York 14627, USA

(Received 28 April 2005; revised manuscript received 2 September 2005; published 21 November 2005)

In contrast to the common belief for femtosecond laser ablation that the thermal energy remaining in the ablated sample should be negligible, we recently found that a significant amount of residual thermal energy is deposited in metal samples following multishot femtosecond laser ablation. This suggests that there might be a significant enhancement in laser light absorption following ablation. To understand the physical mechanisms of laser energy absorption, we perform a direct measurement of the change in absorptance of gold due to structural modification following multishot femtosecond laser ablation. We show that besides the known mechanisms of absorption enhancement via microstructuring and macrostructuring, there is also a significant absorption enhancement due to nanostructuring. It is found that nanostructuring alone can enhance the absorptance by a factor of about three. The physical mechanism of the total enhanced absorption is due to a combined effect of nanostructural, microstructural, and macrostructural surface modifications induced by femtosecond laser ablation. Virtually, at a sufficiently high fluence and with a large number of applied pulses, the absorptance of gold surface can reach a value close to 100%.

DOI: 10.1103/PhysRevB.72.195422

PACS number(s): 68.47.De, 68.35.−p, 79.20.Ds, 68.37.Hk

I. INTRODUCTION

Recently, much research activity has been focused on both physical processes of femtosecond laser ablation and its applications for high-precision materials micromachining, thin-film deposition, generation of ultrashort x-ray pulses, and synthesis of nanoparticles. It is commonly believed that one of the most important advantages of femtosecond laser ablation is that the energy deposited by ultrashort laser pulses does not have enough time to move into the bulk sample. Therefore, the residual thermal energy remaining in the bulk sample should be negligible. Recently, we performed a direct measurement on the thermal energy remaining in bulk metals following multipulse femtosecond laser ablation. In contrast to the previous belief, we found a significant amount of residual thermal energy deposited in various metals. We suspect that an enhancement in absorption following femtosecond laser ablation is an important factor contributing to the enhanced residual thermal energy. However, it is unclear how a femtosecond laser will induce such a noticeable change in absorption.

The absorptance $A$ of a pure metal with a clean surface consists of two components $A_{INTR}$ and $A_{SR}$:

$$A = A_{INTR} + A_{SR},$$

where $A_{INTR}$ is the intrinsic absorptance and $A_{SR}$ is the contribution due to surface roughness. For an optically smooth metal surface, $A_{SR}$ is about 1–2% of $A_{INTR}$ but the role of $A_{SR}$ enhances as the surface roughness increases. For multipulse ablation, only the first femtosecond laser pulse interacts with an undamaged surface, since the laser-induced surface structural modification develops long after the ultrashort pulse. In this case, $A$ is governed by $A_{INTR}$, which can be a function of laser fluence due to laser-induced change in the dielectric constant of the material. All the subsequent laser pulses interact with a structurally modified surface and their absorption is determined by both $A_{INTR}$ and $A_{SR}$. The absorption of a single femtosecond laser pulse by an undamaged metal surface has been studied in the past, where the absorption is dominated by $A_{INTR}$. However, the coupling of laser energy to a metal in multipulse femtosecond laser ablation has not yet been investigated, where $A_{SR}$ may have a significant value due to surface structural modification.

In this paper, we study the effect of surface structural modifications on the absorptance of gold in multipulse femtosecond laser ablation when an originally plane and smooth surface transforms into a blind hole. This effect is investigated as a function of the number of applied ablation pulses at various fluences. To study the absorptance, we apply a laser calorimetry technique, allowing a direct measurement of laser energy absorbed by the sample. We show that femtosecond laser-induced surface modification enhances the sample absorptance that can reach a value close to 100% at a sufficiently high fluence with a large enough number of applied pulses. To understand the physical mechanism of this large enhancement in energy absorption, we also examine the surface modifications using a scanning electron microscope (SEM). We show that besides the known mechanisms of absorption increase via microstructuring and macrostructuring, there is also a significant absorption enhancement due to nanostructuring. It is found that nanostructuring alone can enhance the absorptance by a factor of about 3.

II. EXPERIMENTAL SETUP

In our experiment, we use an amplified Ti:sapphire system generating 60-fs pulses of about 1.5 mJ/pulse at 1-kHz repetition rate and with a central wavelength at 800 nm. The laser beam is focused onto a sample with a 40-cm-focal-length lens at normal incidence. An electromechanical shutter is used to select the number of pulses, $N$, applied to the sample. The absorptance of the ablated spot is studied in the following way. After ablation of the sample with a chosen number of pulses, we reduce the laser fluence...
to a level much below the ablation threshold. Subsequently, we irradiate the ablated spot again using a train of low-fluence laser pulses that will not induce any further surface modification. A certain amount of energy from this low-fluence pulse train, \( E_A \), is absorbed in the skin layer of the sample, dissipates via heat conduction in the sample, and causes its bulk temperature rise, \( \Delta T \). We measure this temperature rise with a thermocouple battery that allows \( E_A \) to be determined calorimetrically as \( E_A = C \Delta T \), where \( C \) is the known heat capacity of the sample. The details of this calorimetric technique have been described elsewhere.\(^\text{10}\) The measurement error for \( E_A \) is estimated to be about 10\%. To measure energy \( E_I \) incident upon the sample, a certain fraction of incident pulse train energy is split off by a beam splitter and measured with a joulemeter. The measurement error of \( E_I \) is estimated to be about 5\%. Having measured \( E_I \) and \( E_A \), the absorptance of the ablated spot can be found as \( A = E_A / E_I \). Laser-induced surface modifications are studied using a SEM and an optical microscope. The sample surface is mechanically polished.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The optical properties of surface modifications are studied following multipulse ablation at single-pulse laser fluences of \( F=1.1, 0.35, 0.17 \), and 0.078 J/cm\(^2\) in air. The ablation threshold \( F_{\text{abl}} \) for a pristine surface is found to be \( F_{\text{abl}}=0.067 \) and 0.048 J/cm\(^2\) for single-pulse and 500-pulse train irradiation, respectively. The numbers of pulses required to perforate a 1-mm-thick sample at the center of the irradiated spot are determined to be 16 100, 25 000, and 77 000 pulses at \( F=1.1, 0.35, \) and 0.17 J/cm\(^2\), respectively. This corresponds to average ablation rates of 63, 40, and 13 nm/pulse, indicating that a single laser pulse produces a nanoscale modification in depth. Plots of absorptance versus the number of ablation shots, \( N \), at different \( F \) are shown in Fig. 1. For an undamaged surface, we can see that the absorptance remains a constant value of 0.12 when measured at \( F=0.0043 \) J/cm\(^2\), which is an order of magnitude below \( F_{\text{abl}} \). The absorptance of a structurally modified surface is significantly greater than that of the undamaged surface and shows dependence on the number of applied ablation pulses, \( N \).

The \( A(N) \) curves for the ablated surface can be characterized into four distinct regions marked with \( A, B, C, D, \) and \( E \) on \( A(N) \) in the case of \( F=0.17 \) J/cm\(^2\) in Fig. 1.

(i) Region \( AB \), where the absorptance initially increases from 0.12 (undamaged surface) to a value in the range of 0.25–0.33. Typically, this region covers the first 1–10 shots. For example, this initial enhancement of absorptance can be produced by four pulses at \( F=0.17 \) J/cm\(^2\) or by one pulse at \( F=0.35 \) and 1.1 J/cm\(^2\). An optical microscopy study shows that the irradiated spot is entirely covered with surface modification following ablation by only one pulse when \( F \geq 0.35 \) J/cm\(^2\), but by four pulses at \( F=0.17 \) J/cm\(^2\). Therefore, the enhancement of absorptance with \( N \) at \( F=0.17 \) J/cm\(^2\) appears due to both the surface modification and an increase in size of the modified area.

(ii) Region \( BC \), where absorptance undergoes a slight decrease as \( N \) increases. Typically, this region covers approximately the next 100–300 pulses. Both regions \( AB \) and \( BC \) extend to a larger number of pulses when the surface is modified at \( F \) only slightly above \( F_{\text{abl}} \) as seen from the curve at \( F=0.078 \) J/cm\(^2\) in Fig. 1.

(iii) Region \( CD \) is characterized by a further enhancement of absorptance with the increase of \( N \). This region extends to \( N \) of an order of 10 000 pulses.

(iv) Region \( DE \), where absorptance reaches the maximum value that does not change with further increase of \( N \).

In order to understand how surface modifications affect absorptance, we take the SEM pictures of surface morphology shown in Figs. 2–6. In \( AB, BC, \) and \( CD \) regions, where absorptance exhibits dependence on \( N \), the following surface modifications are typically observed. For region \( AB \), a characteristic modification is nanoscale roughness (Fig. 2). In region \( BC \), two major features are observed. First, nanoscale roughness develops further in the form of nanobranches [Fig. 3(a)] and spherical nanoparticles [Fig. 3(b)]. Second, microscale structures begin to develop in the forms of microcavities and by variation in the angle of incidence (angular dependence of Fresnel absorption). Nanoscale structural features can affect absorptance since the optical properties of a nanostructured material can be quite different from the bulk.\(^\text{19,20}\) Laser-induced periodic surface structures (LIPSS) may enhance absorption of laser energy via generation of surface electromagnetic waves.\(^\text{13,21}\) It is worthy to mention that the LIPSS observed in our experiment has even finer nanostructural features shown in Fig. 4(b).

Our study shows that the absorption of laser energy in femtosecond laser ablation can also be altered through rede-
position of ablated material. The examination of the black
halo produced around the crater shows that its elemental
composition determined by energy dispersive x-ray analysis
is identical to that for a pristine surface, i.e., the black halo is
a layer of the ablated and redeposited gold. SEM images in
Figs. 5 and 6 demonstrate that the black halo has a structure
of spherical nanoparticle aggregates that is typically seen in
gold-black films.22,23 The gold-black films have been known
for their high absorptance in the infrared.24,25 Therefore, the
gold-black halo can enhance the absorption of low-intensity
wings of the incident Gaussian beam and contribute to re-
sidual heating of the sample.10 Since redeposition of ablated
material occurs both outside and within the ablated spot, the
redeposition of the nanoparticles produced by ablation can
also enhance the absorption of light in the ablated area. For
example, an enhanced absorption of light by a semiconductor
coated with Au nanoparticles has recently been reported.26
Therefore, in femtosecond laser ablation, the enhanced ab-
sorption can occur due to surface nanostructures, microstruc-
tures, macrostructures, and redeposition of nanoparticles de-
pending on ablation conditions. The combined effect of these
surface modifications can lead to virtually 100% absorption
of laser light in multipulse ablation with a sufficiently large
number of pulses at high fluence as shown in Fig. 1.
Previously,10 we have also found that, under the same abla-
tion conditions, almost all incident laser energy is retained in
the sample as the residual thermal energy. This suggests that
the energy carried away by the ablated material is small in
Au, and the enhanced absorptance observed here appears to
be the dominant factor in the enhanced residual thermal en-
ergy deposition observed previously in multipulse femtosec-
ond laser ablation at large numbers of applied pulses.
Since different surface modifications are superimposed on
each other, it is difficult to completely isolate and determine

FIG. 2. SEM images of the Au surface (a) before irradiation and
(b) after 1 shot at $F=1.1\, J/cm^2$. This nanoscale roughness produced
by ablation enhances the absorptance by a factor of 2
(region $AB$ in Fig. 1).

FIG. 3. Nanoscale surface structural features produced at
$F=1.1\, J/cm^2$ (region $BC$). (a) Nanobranches after two-shot abla-
tion. (b) Spherical nanoparticles after five-shot ablation.

FIG. 4. LIPSS produced in irradiated area by 20 000 shots at
$F=0.17\, J/cm^2$ (region $CD$ in Fig. 1). (a) SEM micrograph showing
the period of LIPSS. (b) Nanobranches and supported spherical
nanoparticles in LIPSS.
each individual contribution to the enhanced absorptance. Therefore, we only provide the following estimations on the contributions of nanostructures, microstructures, and macrostructures induced by femtosecond laser ablation. Since surface nanostructures are the dominant feature in region $AB$ and part of region $BC$ for $N < 50–100$ and the absorptance increases from 0.12 to 0.25–0.33 over these regions (see Fig. 1), nanostructures alone account for the additional absorptance increase of about 0.1–0.2. The contribution of two types microscale structures, LIPSS and random roughness, is estimated as follows. To estimate the contribution of LIPSS, we ablate a sample using $p$-polarized light and measure the low-fluence absorptance $A(N)$ of the ablated spot with both $p$ and $s$ polarizations. The curves $A(N)$ of different polarizations are found to be identical, and this indicates that the grating effects of microscale LIPSS on the absorption of laser light is negligible. To estimate the contribution of microscale random roughness, we abrade a mechanically polished sample surface with a sandpaper to produce a rms roughness of $3 \mu m$, which is estimated to be comparable to the laser-induced roughness for $100 < N < 1000$. The absorptance of this abraded surface is then measured to be about 0.24 as opposed to 0.12 for a mechanically polished surface, and this indirectly shows that the random microroughness accounts for the additional absorptance increase of about 0.12. Macrostructures come into play in two major forms, deep central channel and concentric ring grooves, when the number of pulses is roughly larger, 500–1000, and laser fluence is higher than 0.17 J/cm$^2$. Two typical SEM pictures showing macrostructure of craters are given in Fig. 7. The macroscale crater formation starts in region $CD$, and therefore, we believe the progressive increase of macrostructure size largely accounts for the absorptance increase from 0.4 to about 1.0. However, nanostructures and microstructures also develop further in regions $CD$ and $DE$ and may also contribute to absorptance increase to some extent.

### IV. CONCLUSION

In summary, our study shows a significant increase in absorptance of gold due to surface modifications following multipulse femtosecond laser ablation. At sufficiently high fluence and with a large number of applied pulses, the ab-
Enhanced Absorptance of Gold Following Laser Ablation

Thomas M. P. Lodge, Ioannis K. Arvanitis, and John X. H. O’Dwyer

Absorptance can reach virtually 100%. We show that the physical mechanism of the enhanced absorption is due to a combined effect of nanostructural, microstructural, and macrostructural surface modifications induced by femtosecond laser ablation. Besides the physical mechanisms of the enhanced absorption discussed in this paper, our study also contributes to the fundamental understanding of femtosecond laser-matter interactions from the following aspects. First, laser-induced nanostructures alone can enhance the absorptance of Au by a factor of about 3 following only 1-3 pulses. This result suggests a direction for future study of optical properties of nanostructures imprinted on a metal surface. Second, our study finds a type of microscale periodic structure with much finer nanoscale structures following ablation with a large number of applied pulses. This observation may prompt us to reexamine our current understanding of the physical mechanism of periodic structure formation. Third, redeposition of laser-induced nanoparticles is also seen outside of the ablated spot leading to the formation of a nanostructured material known as gold black. Finally, our study also indicates potential applications of femtosecond laser ablation for modifying optical properties of metals and producing technologically valuable surface coatings such as gold-black films.

Acknowledgments

The authors acknowledge J. Dai and B. McIntire for assistance with SEM micrographs. The research was supported by NSF and DARPA administered through ARO.