Investigation of nanoparticle generation during femtosecond laser ablation of metals

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Abstract

The production of nanoparticles via femtosecond laser ablation of gold and copper is investigated experimentally involving measurements of the ablated mass, plasma diagnostics, and analysis of the nanoparticle size distribution. The targets were irradiated under vacuum with a spot of uniform energy distribution. Only a few laser pulses were applied to each irradiation site to make sure that the plume expansion dynamics were not altered by the depth of the laser-produced crater. Under these conditions, the size distribution of nanoparticles does not exhibit a maximum and the particle abundance monotonously decreases with size. Furthermore, the results indicate that two populations of nanoparticles exist within the plume: small clusters that are more abundant in the fast frontal plume component and larger particles that are located mostly at the back. It is shown that the ablation efficiency is strongly related to the presence of nanoparticles in the plume.

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1. Introduction

Nanoparticles are of great interest for many technological applications and fundamental research due to their size-dependent physical properties. They can be formed in different ways and the synthesis of nanoparticles of controlled size is a challenge [1–3]. In fact, almost all natural and laboratory plasmas are sources of nanoparticles. The most prominent examples are interstellar dust [4], thermonuclear fusion [5], and low-pressure radio-frequency discharges [6]. The plasma produced by pulsed-laser ablation using short laser pulses has been shown to be an efficient tool to produce small particles in the nanometer size-range [7–9]. However, little is known about the physical mechanisms involved in the particle formation. Recently, molecular dynamics simulations have been used to analyze short pulse laser ablation [10]. The calculations predict plume composition, kinetic energies of species, and the size distribution of nanoparticles at the early stage of plume expansion. However, experimental results suitable for the validation of these theoretical findings are still lacking. In the present paper, we present a detailed analysis of the plume formed by femtosecond laser ablation of gold and copper, two metals having very different electron-lattice coupling coefficients (see Table 1). Both fast imaging and time and space resolved optical emission spectroscopy were used to identify the plume species and to measure their expansion velocities. In addition to optical analysis, the ablated mass was determined by measuring the volume of the laser-produced craters using optical microscopy. Furthermore, the nanoparticle size distribution was deduced from atomic force microscopic (AFM) analysis of particles deposited on mica substrates. The parametric study performed in well defined experimental conditions allows for several conclusions on the nanoparticle formation mechanisms. In particular, the influence of irradiation conditions and material properties on the nanoparticle size distribution and production yield is investigated.

2. Experiment

Ablation experiments were carried out with a Ti:Sapphire laser (Spectraphysics, model Hurricane) delivering pulses of 100 fs duration at a repetition rate of 1 kHz. The laser was operated at 800 nm. An aperture of 2 mm diameter was employed to select the centre part of the Gaussian beam which...
The ablated material was deposited on mica substrates, placed parallel to the target at a distance of 20 mm from the target surface. It was analyzed by atomic force microscopy in the semi-contact mode. Several areas of 2 μm × 2 μm dimension were scanned to characterize each deposit in order to count a number of particles sufficiently large for statistical analysis of the particle size distribution.

3. Results and discussion

Plume images recorded during laser ablation of gold and copper are shown in Fig. 1 for different time delays \( t \) between the laser pulse and the observation gate of 20 ns duration. Each image was obtained by accumulating the signal over several ablation events. For a maximum number of 160 ablation events, 8 sites were irradiated with 20 laser pulses. To enhance the presentation quality, the intensity matrix was smoothened by using an appropriate procedure. The images recorded at \( t = 200 \) and 400 ns reveal the presence of two plume components. A “slow” component of high intensity is located close to the target whereas a “fast” component of lower emission intensity is observed at larger distance. To visualize the “fast” plume component, the 10-level grey scale colour palette is adjusted to the emission intensity of this component. Thus, the “slow” component is strongly saturated and the observed shape does not represent the spatial distribution of the emission intensity. Both plume components have different expansion dynamics. The fast component separates from the target surface whereas the slow component remains in contact with the target surface, even for times larger than tens of microseconds. The expansion behaviour of the slow component is attributed to particle size and temperature gradients. In fact, the numerical simulations [10,14] predict particles of larger size and lower temperature in the rear part of the plume, whereas smaller and hotter particles are expected in the frontal part. According to Fig. 1, the expansion velocities of both components are larger for copper than for gold, which is linked to the difference in atomic weight (see Table 1).

The intensity distribution versus wavelength and distance from target \( z \) is presented in Fig. 2 for ablation of copper. A

![Fig. 1. Plume images recorded during ablation of gold and copper for several times and a laser fluence of 4 J cm\(^{-2}\).](image_url)
delay of 20 ns was applied between the laser pulse and the observation gate of 5 ns duration. The recording was performed by accumulating the signal over 640 ablation events (32 irradiation sites submitted to 20 laser pulses). The spectral range from 484 to 495 nm was chosen to observe simultaneously spectral lines of both, atomic and ionized copper. Close to the target surface (z = 0), a continuum emission is detected.

Similar observations of continuum emission were made by other authors during femtosecond laser ablation of different metals. According to these studies, the black-body like continuum is associated to the presence of hot nanoparticles within the ablation plume [15–17]. Thus, the slow component in the plume images presented in Fig. 1 consists mainly from nanoparticles. At slightly larger distance, spectral lines of neutral atoms are identified in Fig. 2. This emission corresponds to the fast plume component. The signal detected below the target surface (z < 0) is due to the reflection of radiation by the target surface. In addition to the two components observed in the plume images, the spectroscopic measurements allow the detection of a third component formed by ions. This component is not observed in the plume images when the spectrally integrated intensity of ionic emission is small with respect to that of the other plume components. The \( H_\beta \) spectral line emission is attributed to the presence of hydrogen on the target surface. The residual hydrogen within the vacuum chamber is due to the relative high background pressure of \( 10^{-4} \) Pa. The spectroscopic analysis during gold ablation did not allow for the detection of Au\(^+\) spectral lines. The low yield of gold ions below the detection limit of our spectroscopic apparatus is attributed to the high ionization potential of gold atoms that is about 1.5 eV larger than that of copper (see Table 1).

The ablation rate, that is the ablated depth per laser pulse, was measured in the following way: for each laser fluence value, a series of 20 craters was drilled with an increasing number of applied laser pulses. According to the linear increase of crater depth \( z \) with the laser pulse number \( n_{\text{las}} \), the ablation rate was deduced from the slope \( \Delta z / \Delta n_{\text{las}} \). The ablation rate as a function of laser fluence is shown in Fig. 3 for femtosecond laser irradiation of both, copper and gold. Ablation rate values from literature [18] are also inserted for copper. A good agreement between the present data and those of Nolte et al. is noted although the laser pulse durations in both studies were different (150 fs in Ref. [18]). That indicates that the ablation rate is almost independent of the laser pulse duration as long as the latter is much smaller than the electron-lattice relaxation time (see Table 1).

In addition to the ablation rate, the plume emission intensity is displayed in Fig. 3. These results are obtained by integrating the plume emission intensity over the entire image recorded for a delay of 400 ns. It is observed that the plume intensity is almost proportional to the ablation rate. In the case of an optically thin plasma, the plume intensity increases linearly with the number of emitters. This indicates that the plume temperature is almost independent of the applied laser fluence.

We define the ablation efficiency as the number of ablated atoms per unit of incident laser pulse energy. For ablation with a uniform energy distribution, the ablation efficiency is given by

\[
\varepsilon_{\text{ablat}} = \frac{\Gamma_{\text{ablat}} \times \rho}{m_a},
\]

Here \( \Gamma_{\text{ablat}} \) is the ablation rate, \( \rho \) and \( m_a \) are the specific mass and atomic weight of the metal target, respectively. The ablation efficiency of gold is presented in Fig. 4 as a function of laser fluence. A strong increase of \( \varepsilon_{\text{ablat}} \) is observed for small laser fluence values from the ablation threshold up to 0.7 J cm\(^{-2}\), where the ablation efficiency reaches its maximum. For larger fluence values, \( \varepsilon_{\text{ablat}} \) decreases slowly.

The atomization stage of the plume is defined as the ratio between the atomized mass and the total ablated mass. As atoms dominate in the fast plume component and nanoparticles in the slow one, the atomization stage is related to the intensity
Fig. 4. Ablation efficiency and atomization stage of gold as a function of laser fluence. The dashed line stands for the ablation efficiency that is expected for thermal evaporation. The atomization stage was estimated from the intensity ratio $I_{\text{atoms}}/I_{\text{tot}}$, where $I_{\text{atoms}}$ and $I_{\text{tot}}$ were deduced from the same kind of images as those used in Fig. 3.

The ratio between the plume components by

$$\Lambda = \frac{M_{\text{atoms}}}{M_{\text{atoms}} + M_{\text{nps}}} \approx \frac{I_{\text{atoms}}}{I_{\text{atoms}} + \alpha I_{\text{nps}}}.$$  \hspace{1cm} (2)

Here $M_{\text{atoms}}$ and $M_{\text{nps}}$ are the ablated masses in form of atoms and nanoparticles, respectively. The intensities $I_{\text{atoms}}$ and $I_{\text{nps}}$ correspond to the fast and the slow plume components, respectively. The numerical value $\alpha$ takes into account the fact that radiation from atoms and nanoparticles is generated through different mechanisms. Assuming $\alpha = 1$, the atomization stage corresponds to $\Lambda = I_{\text{atoms}}/I_{\text{tot}}$, where $I_{\text{tot}}$ is the total intensity of the plume.

The atomization stage for ablation of gold is presented in Fig. 4 as a function of laser fluence. It has its maximum value for a laser fluence close to the ablation threshold and strongly decreases up to a minimum value that is obtained for $F_{\text{las}} = 0.7 \text{ J cm}^{-2}$, where the ablation efficiency has its maximum. The further increase of laser fluence leads to a slow increase of the atomization stage. Thus, there exists a strong correlation between the ablation efficiency and the atomization stage that is attributed to the fact that a total atomization requires more energy than the decomposition of matter in nanoparticles. The laser fluence corresponding to the maximum ablation efficiency and to the minimum atomization is supposed to be the result of the target-heating regime. Close to the threshold fluence (see Table 1), the cooling after laser heating is faster and only the first atomic layers can escape from the target. The atomization stage is large due to the high temperatures in the region close to the target surface. The ablation efficiency is low as the energy loss due to heat diffusion towards the bulk material is large. When increasing laser fluence, more material from the subsequent atomic layers can escape the target. As deeper layers have lower initial temperatures, they are not fully atomized and escape the target in the form of a mixture of gas and liquid (nanoparticles). Thus, the ablation efficiency increases, whereas the atomization stage diminishes. For $F_{\text{las}} > 0.7 \text{ J cm}^{-2}$ the characteristic time of ablation becomes longer, and the cooling due to classical heat diffusion prevents the further increase in the ablation depth. Thus, the ablation efficiency decreases slowly, whereas the atomization stage slightly rises. It is noted that the intensity ratio $I_{\text{atoms}}/I_{\text{nps}}$ was always much larger for copper than for gold (see, i.e. Fig. 1) indicating thus that the atomization stage increases with the electron-lattice coupling coefficient.

The plume intensity distribution as a function of distance $I(z)$ is shown for different time delays in Fig. 5. The recordings correspond to copper ablation with $F_{\text{las}} = 4 \text{ J cm}^{-2}$. The $I(z)$ curves were obtained from the plume images by averaging the signal over several pixel rows around the plume symmetry axis as indicated in Fig. 1 for copper at $t = 10 \mu\text{s}$. The $I(z)$ curves for $t \leq 300 \text{ ns}$ (a) and $t \geq 2 \mu\text{s}$ (b) correspond to the time-of-flight distributions of atoms and nanoparticles, respectively.

To characterize the expansion of both plumes, the distance of the “centre-of-mass” intensity

$$z_{\text{CM}} = \left[ \frac{\int z I(z) \, dz}{\int I(z) \, dz} \right]$$  \hspace{1cm} (3)

was determined for each delay and the characteristic expansion velocity was deduced from the slope $\Delta z_{\text{CM}}/\Delta t$. The distance of maximum intensity $z_{\text{CM}}$ versus time is presented for atoms and nanoparticles in the insets of Fig. 5(a and b), respectively. Fig. 6 shows the characteristic expansion velocities of atoms (a) and nanoparticles (b) that were deduced from the plume intensity profiles as shown in Fig. 5. In addition, the velocity of copper ions is shown in Fig. 6. The Cu$^+$ velocity was deduced from the spectrally resolved images (see Fig. 2) by determining the slope $\Delta z_{\text{CM}}/\Delta t$ similar to the velocity measurement of neutral atoms and nanoparticles.

For neutral atoms of gold and copper (a), a strong increase of the propagation velocity with the laser fluence is observed near the ablation threshold. The velocity rise is progressively reduced when increasing the laser fluence. It remains almost constant for $F_{\text{las}} > 1 \text{ J cm}^{-2}$. It is noted that the corresponding kinetic energies of the atoms are almost equal for gold and copper. For $F_{\text{las}} = 4 \text{ J cm}^{-2}$, one has $u_{\text{Cu}} = 8.9 \times 10^3 \text{ m s}^{-1}$ and
\( u_{Au} = 5.4 \times 10^3 \text{ m s}^{-1} \) corresponding to kinetic energies of 27 and 29 eV, respectively. The behaviour of the nanoparticle velocity versus laser fluence (b) is different from that of the atom velocity. Near the ablation threshold, a slight decrease in velocity with laser fluence is observed. For larger \( F_{\text{las}} \)-values, the nanoparticle velocity is almost constant. The weak dependence of the propagation velocities of both atoms and nanoparticles for larger laser fluences indicates that, during the initial stage of plume expansion, the mean temperature of the ablated matter is almost independent of \( F_{\text{las}} \). A weak influence of laser fluence on the plume temperature was also expected from the proportional increase of plume intensity with the ablation rate (see Fig. 3), as the emission intensity strongly depends on the plume temperature (\( I \propto T^4 \)). The velocity increase of atoms near the ablation threshold is supposed to be due to the increase of the ablated material quantity and the associated changes during the adiabatic expansion phase. The decrease in the nanoparticle velocity near the ablation threshold can be explained by the change in the nanoparticle size distribution. For an almost constant temperature, the decrease in the average size of particles leads to a larger expansion velocity of the nanoparticle plume.

According to the time- and space-resolved measurements of the nanoparticle temperature, it is expected that the particles arrive on the substrate in the liquid state [20]. As the particles are of sizes in the nanometer range, their shape after the impact on the substrate depends only on the angle of contact mica–metals. This angle being very high for the interface mica–metals (\( \sim 120^\circ \) for gold on silica [21]), the particles are expected to become almost spherical after their impact on the substrate. Thus, the particle height measured via AFM analysis is close to the size of the almost spherical particles. The relative abundance of nanoparticles versus particle size is presented in Fig. 7 for ablation of copper with \( F_{\text{las}} = 4 \text{ J cm}^{-2} \). It was obtained from AFM analysis of three areas of \( 2 \mu\text{m} \times 2 \mu\text{m} \) dimension including an overall number of 1100 particles. A typical AFM image corresponding to one of the analyzed areas is shown in the inset. To get the particle size distribution, a size step of 0.5 nm was applied as shown in Fig. 7. The relative abundance was obtained by counting the number of particles for each interval and normalizing the total number to 100%. It is noted that the analysis does not take into account particles of sizes smaller than 1 nm. Thus, in the range of analysis, the relative abundance is a monotonously decreasing function of particle size. More detailed information on the particle size distribution is given in Fig. 8 where the particle abundance versus size is presented on a logarithmic scale for three different \( F_{\text{las}} \)-values. Here, two populations of nanoparticles can be identified. Small particles (\( d < 7 \text{ nm} \)) are characterized by a size distribution that varies as \( f(r) \propto r^{-A} \), where \( r = d/2 \) is the particle radius and \( A \) a numerical constant. The latter
diminishes when the laser fluence increases showing thus that the number of larger particles rises. This result has been predicted above from the expansion behaviour of the nanoparticle plume. The larger velocity near the ablation threshold (see Fig. 6) has been attributed to the change in the particle size distribution towards smaller sizes. Furthermore, it is shown in Fig. 8 that the particles larger than 7 nm are characterized by a size distribution \( f(r) \propto r^{-3.5} \). This distribution is known to be established in all natural and laboratory plasmas when a sufficiently large number of fragmenting collisions occurs. That distribution was first observed in interstellar dust and theoretically described by Plummer [22]. The smaller particles are expected to be either directly ejected from the target, or formed by condensation reaction in the plume. The size distribution of gold nanoparticles and its variation with laser fluence (not shown here) were found to be very similar to the results presented in Fig. 8 for copper.

4. Summary and conclusions

The present experimental study on femtosecond laser ablation of copper and gold allows for several conclusions on the laser ablation and nanoparticle formation mechanisms. Precise measurements of the ablation rate for various \( F_{\text{las}} \)-values allowed for the determination of the ablation efficiency as a function of laser fluence. The ablation efficiency was shown to be strongly correlated to the atomization stage of the ablated matter that was deduced from plume analysis using fast imaging and optical emission spectroscopy. Indeed, the ablation efficiency reached its maximum value for \( F_{\text{las}} = 0.7 \text{ J cm}^{-2} \) where the relative amount of ablated mass in form of nanoparticles was maximum (minimum of atomization stage). In addition, the measured ablation efficiency was always much larger than the value one would expect for complete atomization in the case of thermal vaporization. Thus, a large amount of nanoparticles is supposed to be directly emitted from the target. Analyses of the nanoparticle size distribution via atomic force microscopy indicate that two populations of nanoparticles exist within the plume. Particles smaller than 7 nm are supposed to be directly emitted from the target, whereas larger particles are expected to be formed by collisions. The size distribution for larger particles agrees with the \( r^{-3.5} \)-dependence. It is furthermore shown that the increase of laser fluence favours the formation of larger particles with respect to smaller ones. Contrarily to the results reported by other authors [8,9,16], no maximum is observed in the particle size distribution and the particle abundance is a monotonously decreasing function of particle size in the laser fluence range up to 5 J cm\(^{-2}\). The difference in the intensity ratio of atomized and nanoparticle plume emission that was observed for ablation of copper and gold indicates that the atomization stage increases with the electron-lattice coupling coefficient. However, no significant difference between the nanoparticle size distributions generated from copper and gold targets was observed. The presented experimental results agree with the results of recent combined molecular dynamics-direct Monte Carlo (MD-DSMC) simulations [14]. These calculations account for nanoparticle ejection from the target as well as for the following particle evaporation, growth, and fragmentation in collisions during the plume expansion. The calculation results in vacuum also predict a particle abundance that monotonously decreases with size.

References