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Scanning the laser beam for ultrafast pulse laser cleaning of paint

**A.V. Rode · D. Freeman · K.G.H. Baldwin · A. Wain ·
O. Uteza · Ph. Delaporte**

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Abstract Powerful ultrafast femtosecond laser pulses have the unique ability to ablate material with minimal collateral damage. This ability offers the potential for new applications of ultrafast lasers for removing surface contamination and unwanted surface layers in the conservation of artworks and heritage objects. In this paper we concentrate on the problem of precise and fast scanning of the laser spot over the treated surface for cleaning relatively large surface areas. Preliminary results are presented for the removal of intrusive paint layers, using a 12-ps laser with 1.5 MHz repetition rate, and 0.5 ps laser with 10 kHz repetition rate.

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1 Introduction

Laser ablation with ultrafast laser pulses possesses a unique ability to remove thin submicron surface layers without generating heat or shock waves in the bulk of the material. This is due to the very fast delivery of electromagnetic laser energy into the surface layer, which occurs too quickly for the absorbed laser energy to be transferred into the bulk material through heat conduction or shock wave propagation [1–4]. As a result, a heated surface layer is ablated while the bulk of the material remains cold.

The pulse duration required to remove a surface layer in this non-equilibrium, short-pulse regime of ablation depends on the properties of the material to be ablated, such as heat diffusion, thermal capacity, ionization energy and density, as well as electronic and optical properties [1, 4]. In general, the pulse should be shorter than the electron-lattice equilibration time and the heat diffusion time from the surface layer. This usually lies in the picosecond to sub-picosecond time domain. The thickness of the layer removed at the laser fluence just above the ablation threshold is of the order of 100 nm per pulse.

The advantages of using ultrafast lasers for micromachining (precise removal) of surfaces have already been proven in applications such as dentistry and eye surgery, which are also very sensitive to collateral damage [5–8]. Compared to long-pulse nanosecond lasers, femtosecond lasers offer higher etching resolution, absence of collateral damage and minimal photochemical modification of the surface. These qualities have opened up new possibilities in the cleaning of sensitive and technically demanding artworks and other objects of historical and cultural importance [9].

Currently, however, the application of femtosecond lasers to the cleaning of artifacts has been limited to small surface areas and to a limited volume of ablated material, of the order of a few mm^3 at most. This is due to the fact that the low energy of the ultrashort laser pulse requires tight focusing to achieve the required ablation threshold intensity, which is of the order 10^{11}–10^{12} W/cm^2. Moreover, the

A.V. Rode (✉) · D. Freeman
Laser Physics Centre, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia
e-mail: avr111@rsphysse.anu.edu.au

K.G.H. Baldwin
Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

A. Wain
Collection Services Section, The Australian War Memorial, Canberra, ACT 2601, Australia

O. Uteza · Ph. Delaporte
Lasers, Plasmas and Photonic Processes, CNRS—Mediterranean University, Marseille, France

lower ablated mass per pulse, when compared with conventional long-pulse laser-cleaning techniques, requires a significant increase in the laser repetition rate to achieve a reasonable rate of surface treatment. A technique is therefore required to provide fast, precise scanning of the laser beam over the surface area to be treated.

In this paper we analyse the potential advantages and challenges of using ultrafast laser pulses for precise removal of surface layers, and present preliminary results on using ps and sub-ps lasers to remove paint for the conservation of artworks and heritage objects.

2 Laser scanning system

2.1 Scanning requirements

A key requirement for precise removal of surface layers of sub-micron thickness is a high degree of control over the scanning of the focused laser beam. There are several general requirements for scanning systems for the short-pulse high-repetition-rate laser ablation technique:

i. precise control of the ablated depth down to as low as 10 nm/shot requires that each laser shot be located at a fresh point on the surface;
ii scanning along the surface should be faster than the propagation of the heat wave, to avoid heat accumulation;
iii the beam should move with a constant speed over the target surface;
iv. the scanning pattern should cover the surface uniformly, so that every surface point is given the same exposure;
v. the spot size and shape should be the same across the entire scanning pattern.

The first and second requirements lead to a relatively high scanning speed $v = d_{foc} \times R_{rep}$, where d_{foc} is the focal spot diameter, and R_{rep} is the laser repetition rate. For organic materials with thermal diffusivity D of the order of 10^{-2} cm^2/s and with 1 MHz repetition rate the speed is typically

$$v_{scan} = l_{th} \times R_{rep} = \sqrt{D R_{rep}^{-1}} \times R_{rep} > 1 \text{ m/s}, \tag{1}$$

where l_{th} is thermal wave propagation length between the laser pulses. This scanning speed can be obtained relatively easily with an orthogonal pair of galvanometer scanners located at a suitable distance from the target. The third and forth requirements lead to an even coverage of the surface by the scanning laser spot, so that the number of laser pulses per unit area is constant. Galvanometer scanners typically consist of a mirror mounted to an electric motor, with positional feedback supplied to the driver circuit. Under closed-loop operation, a return spring is unnecessary, since the drive electronics can accurately apply the required torque to start and stop the mirror even for a sudden jump in position. Proper tuning of the driver is essential, particularly when different mirrors are fitted.

The fifth requirement, for a beam of constant size and shape, can be achieved with a telecentric scanning lens. Such a lens is designed so that the laser beam strikes normal (perpendicular) to the work surface over the entire scanning field. This can also be achieved with conventional long-focus lenses by placing the scanning mirrors after the focusing lens so that the difference in optical path of the deflected beam is within the lens caustic; however, this is at expense of the tight focusing required for low-energy short pulses.

2.2 Constant velocity alternating spiral

The scanning pattern must be chosen so as to respect the limitations of each scanner; namely, the maximum acceleration (given by the available torque and the moment of inertia of the motor and mirror), and the maximum power dissipation in the motor windings (governed by the average magnitude of acceleration throughout the pattern). One should therefore avoid patterns that involve sharp corners, such as raster scanning, unless a fast beam blanker is available to allow "dead time" for a safer acceleration without uneven illumination of the target. While it is feasible to use a "polygon" scanner for the fast axis of a raster pattern, achieving yet higher scanning speeds, there is still a problem at the edges of the scan lines: the beam is split between the end of one line and the start of the next, destroying the quality of the focused spot and reducing the fluence below the threshold for electrostatic ablation, so that a fast blanker would still be required. Blanking an ultrafast laser at high average and peak powers is not a trivial proposition, so we have used an alternative pattern for our work. A smooth and continuous spiral pattern, alternating between increasing and decreasing radius, has no corners and provides continuous scanning at a constant linear speed with nearly uniform coverage and no wasted dead-time (Figs. 1 and 2). It suffers, however, from the disadvantage of a hole in the center, which is required to limit the acceleration at small radii.

The scanners were computer-controlled as follows. The path was traced at a constant linear speed v_{scan} by generating a pair of analogue waveforms, which were sampled at discrete time intervals (10 µs). The sample points were computed at the target, and converted to deflection angles for the scanners $\pm 40°$ using the optical distance from each scanner to the target, and then output using 16-bit digital-to-analogue converters, resulting in angular steps of $80°/2^{16} = 21.3$ µrad. The outward spiral curve used, expressed in polar coordinates (r, θ), is:

$$r = \frac{p}{2\pi}\theta, \tag{2}$$

where p is the pitch, the radial distance between successive turns; here the pitch is larger than the focal spot. The value of θ at each sample time was computed using a discrete integration of the angular velocity determined at the preceding sample time. The angular velocity of this curve is given by:

$$\frac{d\theta}{dt} = \frac{2\pi v_{\text{scan}}}{p(\theta^2+1)^{1/2}}. \quad (3)$$

When the radius had reached the maximum allowed, the spiral changed to the inward type in which the radius decreased with further increase of angle, until the desired inner radius was reached and the next outward spiral began. Since the angular frequency (and therefore scanning mirror acceleration) is greatest at the center of the pattern, the radius of the central hole must be large enough to respect the limitations of the scanners as described above, or else the pattern would become distorted, with non-uniform speed and area coverage at the center. To ensure the individual spiral traces were not visible in the final result, a small arc $\Delta\theta$ was included at the outermost radius to produce a suitable angular offset between successive spirals, resulting in uniform coverage after a large number of spirals had been traced. This pattern has been the most successful to date in our laser deposition experiments [1, 10].

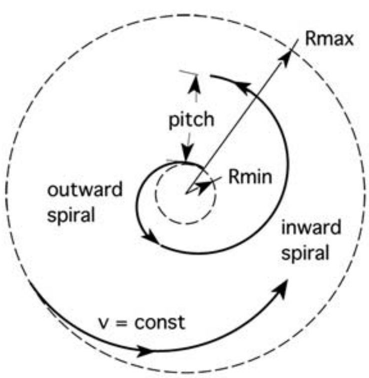

Fig. 1 Scheme for a constant scanning velocity alternating spiral pattern. This is the most suitable for fast scanning of the laser beam due to the absence of sharp turning points

Keeping the laser parameters constant on the surface to be treated is another challenge. To treat an uneven surface the confocal parameter (the depth of focus) should be longer than the surface profile variations. The longer the focal length of the focusing optics and the smaller the numerical aperture, the longer the confocal parameter, which converts into a larger focal spot and lower laser fluence. To compensate the loss in fluence, which must be above the threshold value, one needs to increase the energy per pulse. This can only be achieved by increasing the average power of the laser used, or by reducing the repetition rate.

3 Ablation experiments

Two laser systems were used to perform ultrafast laser ablation of paint. The aim of the tests was to analyse the effectiveness of ultra-fast laser ablation in the removal of paint from firstly an underlying paint layer, and secondly a metal surface. One laser used was a Nd:YVO_4 laser, designed and built at the Australian National University for applications in micro-machining and the deposition of optical thin films [11]. This laser produces an average power of 50 W in 12-ps pulses at a rate of 1.5×10^6 pulses per second and was converted to the second harmonic ($\lambda_2 = 532$ nm). As second laser used was a commercial Yb:YAG laser from 'Amplitude Systems' which generates 500-fs pulses at a rate 10^4 pulses per second; this laser was converted to the second harmonic ($\lambda_2 = 515$ nm). The experiments were conducted with a light-grey ZnO based paint.

The first series of experiments aimed to determine the required speed of scanning. Laser beams were directed to a painted metal target via a telescentric lens, and focused to a spot size of 20 µm (532 nm) and 35 µm (515 nm). The laser was then scanned in a constant velocity 'moving race track' pattern with a size of 20 mm (532 nm) and 2 mm

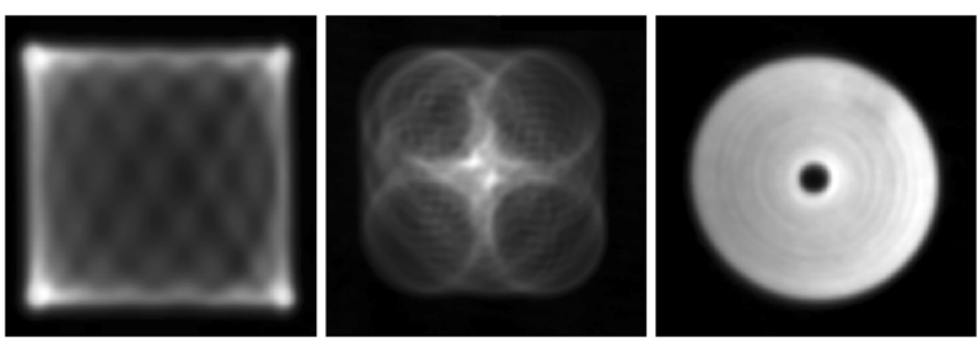

Fig. 2 Laser scanning patterns: Lissajous figure (*left*), Lissajous figure superimposed on a circle (*center*), and an expanding/collapsing spiral (*right*). Clearly, the spiral pattern provides the most uniform coverage, although it has a hole in the center. The images are experimental results obtained by scanning onto a paper diffuser and acquiring an image using a CCD camera with a long integration time

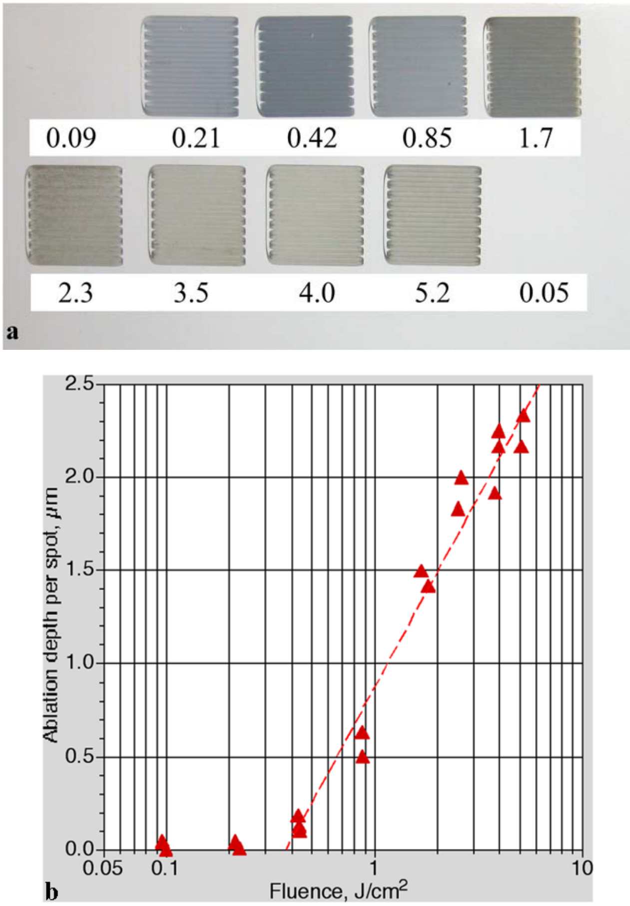

Fig. 3 Racetrack scanning patterns (**a**) at various laser fluences from 0.09 to 5.2 J/cm^2 (the numbers under the patterns are fluences in J/cm^2); and the ablation rate (**b**) of paint with 532 nm 1.5 MHz laser scanning with a speed of 10 m/s or 3 shots per spot

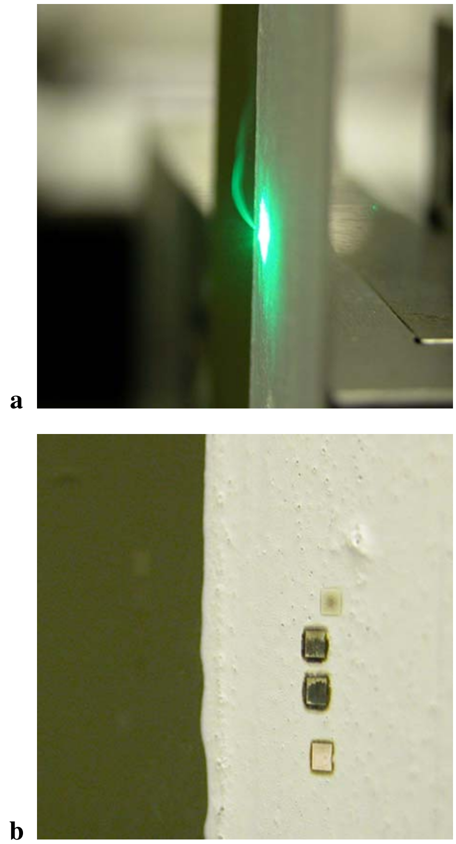

Fig. 4 Ablation of paint using 515 nm 500 fs laser pulses with various scanning speeds of 1 shots per spot (*top pattern* in (**b**), 10 shot/spot (*bottom pattern*), and 100 shot/spot (*two middle patterns*). Ablated vapor (**a**) and re-deposition of debris (**b**) can be clearly seen at the edges of the treated areas at the scanning speed of 10 shots/spot and 100 shots/spot

(515 nm) (Fig. 3a). The race-track pattern was chosen as a compromise to avoid the hole in the middle of the pattern but still preserve the constant scanning velocity over the linear tracks of the pattern.

It was clear from the experiments that a slow scanning speed above 3 shots per spot led to re-deposition of debris and decomposed vapor near the ablated area (see the vapor scattering of the laser light in Fig. 3a, and dark rims around the ablated area in Fig. 4b). This undesired effect with slow scanning was due to absorption of the laser radiation in the ablated vapor and possibly, due to accumulation of heat, as the effect was not observed with a fast scanning speed above 0.35 m/s corresponding to 1 shot/spot exposure with 10^4 Hz repetition rate laser and ~20 m/s with 1.5×10^6 Hz repetition rate.

The second series of experiments aimed to measure the ablation threshold F_{th}. The ablation threshold was determined in a standard way [3, 4] by fitting the semi-logarithmic dependence of the ablated depth per pulse and approximating the curve to a single atomic layer thickness, which was taken to be of the order of 0.3 nm (Fig. 3b). The ablation threshold was found to be 0.25 ± 0.1 J/cm^2 for 12-ps pulses, and $\sim 0.1 \pm 0.05$ J/cm^2 for 500 fs pulses. We noted, that with both 500 fs and 12 ps pulses significant color changes were observed at the fluence close to, but lower the ablation threshold where $F \sim 0.5 F_{th}$. There was no discoloration at the laser fluence below $0.5 F_{th}$ (#37, Fig. 3a).

4 Conclusions

High precision treatment of surfaces and minimum invasiveness are the main advantages of using short-pulse, high-repetition rate lasers for laser cleaning. Contaminant material can be removed in individual layers of precise depth, with sub-micron precision. However, the need for tightly focused, low-energy laser pulses introduces new challenges in precise manipulation of the laser beam.

We demonstrate here that scanning patterns and the scanning speed of the laser beam are important issues in laser cleaning of surfaces with high repetition rate, ultrashort laser pulses. The morphology of the ablated areas strongly depends on the homogeneity of the scanning pattern, while the short time between pulses leads to a need for a relatively high scanning speed. To avoid thermal accumulation the speed of scanning should also be faster than the heat diffusion rate, which for most organic materials is above 1 m/s. We show that a constant velocity alternating spiral and its modification, a moving racetrack pattern, provide the best practical options for homogeneous coverage of the treated area.

In spite of the obvious advantages of applying ultrafast, high-repetition-rate lasers to the conservation of artworks and heritage objects, there are still a few issues to be addressed. For instance:

- Using a top-hat profile for the laser beam will further improve the uniformity of the surface illumination and the morphology of the treated area;
- Fast removal of the ablated vapor is required to avoid redeposition of ablated material;
- Laser beam delivery and precise focusing for cleaning of three-dimensional objects;
- Ultrafast lasers must be optimized for use in conservation, as to date they have only been used in experimental facilities and are prohibitively expensive.

Nevertheless, with the rapid development of powerful and compact femtosecond lasers, ultrafast laser ablation has the potential to become a standard tool in the conservation armory and a key technique for conserving some previously untreatable artworks and heritage objects.

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