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(54) **Title:** METHOD AND APPARATUS FOR FAST QUANTITATIVE ANALYSIS OF A MATERIAL BY LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

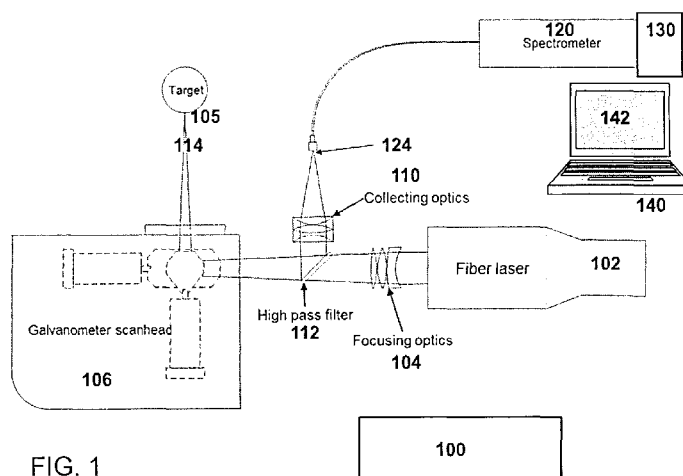


FIG. 1

(57) **Abstract:** The invention discloses an apparatus and method for use with Laser Induced Breakdown Spectroscopy (LIBS) systems that can be applied to the real time analysis of various materials. The invention, in one aspect, provides a layer-by-layer method to remove the undesired coating layer of a material in which a pulsed laser is coupled with high speed scanning optics. To prepare the surface for LIBS, (i) a pulsed laser beam is scanned over an area of the surface to ablate the surface coating layer; (ii) the laser parameters are changed again (i.e. pulse duration is made smaller) and the area scanned again to polish the surface; and (iii) the laser parameters are changed again (i.e. pulse duration is made smaller yet again) and the area scanned again with spectrometric analysis of the plasma plume created by the laser (i.e. LIBS is performed).



METHOD AND APPARATUS FOR FAST QUANTITATIVE ANALYSIS OF A MATERIAL BY LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

Field of the Invention

5 This invention relates to a method and apparatus for preparing the surface of a material for a LIBS measurement. In particular, the invention is directed to a method and apparatus used to remove the undesired coating layer of a material in order to allow for an accurate and real time analysis of the bulk material using LIBS.

10

Background of the Invention

LIBS is a well-known analytical technique for determining the constitution of a sample material that involves focusing a laser beam onto the surface of the sample with high enough power density (i.e. irradiance) to
15 vaporize and ionize a small part of the sample material to produce a plasma or spark having an elemental composition representative of the material. Optical emissions from the plasma plume are collected with light collection optics, and the spectral distribution (i.e. intensity as a function of wavelength) of the collected optical emissions is analyzed in a spectrometer that produces
20 information in electronic form describing the spectral distribution. Since atomic and molecular constituents of sample materials have characteristic optical emission spectra, the information produced by the spectrometer forms a fingerprint of the sample material, revealing the constituents of that part of the sample onto which the laser beam was focused. Plasmas and sparks are
25 used interchangeably in this specification.

LIBS provides rapid, *in situ*, compositional analysis without touching the surface and is now employed in a wide range of applications such as, for example, the monitoring of active agents in pharmaceutical pills, the sorting of materials for recycling, the analysis of soil to determine its impurities and
30 fertilizer content, and the determination of the composition of molten metallic

alloys. The major challenge for these industries is increasing productivity, reducing costs, and maximizing benefits from existing equipment.

The elimination of sample preparation allowing rapid and direct analysis is generally extolled as an advantage of LIBS, especially for quantitative analysis. Material surfaces, however, generally comprise an oxide coating layer or a coating layer containing nitrate, slag, paint, oil, etc. that is not representative of the bulk material to be analysed. To use LIBS to analyse the bulk material, it is first necessary to remove the coating layer. Prior art methods are based on site-by-site analysis involving mechanically cutting or boring a hole into the material at one site using a mechanical drill or using a laser to ablate or clean the layer and expose the bulk material beneath, and then performing the LIBS analysis (see *Laser cleaning in conservation of stone, metal, and painted: state of the art and new insights on the use of the Nd:YAG lasers*, S. Siano *et al.*, Appl. Phys. A (2012) 106:419–446). The site-by-site method has a number of problems that make representative sampling of the bulk material difficult and prevents one from realizing real-time analysis using LIBS.

For example, the energy distribution within the laser beam (typically a near Gaussian mode in many laser systems) used to clean or ablate the coating layer produces cone-shaped craters with non-negligible edge contribution to the ablated mass. The plasma produced by the laser also interacts with the wall of the crater and induces some mixing of material, which complicates the analysis by LIBS and impacts analytical precision and accuracy, in particular in the region close to an interface. Another problem is the limited thickness of the ablated mass by the laser pulses in the nanosecond regime which is in the order of a few tens of nanometers on, for example, metals. Although appropriate to use for cleaning/ablating coating layers having a thickness of a few micrometers, such methods cannot be used for coating layers having a thickness of a few hundred of micrometers or more due to the time required which prevents one from doing a fast analysis by LIBS. Lack of or poor sensitivity as compared to other analytical schemes is

also a problem with using LIBS in this context. In fact, the large background emission (continuum radiation) of the hot laser-induced plasmas can mask and reduce the signal-to-noise ratios of the atomic emission signal from the analyte species, resulting in a lack of or poor sensitivity.

5 Several solutions have been proposed to remedy existing problems. In *Vadillo and Laserna* (J. Anal. At. Spectrometry, vol. 12, 1997, p. 859), it was proposed to improve the depth resolution of LIBS measurements by using a simple two-lens telescope combined with a pinhole mask to generate a collimated output of a XeCl excimer laser, resulting in a flat energy profile.

10 Beam masking was also proposed to attenuate the shot energy and to eliminate the peripheral irregularity of the beam profile (see Kanicky *et al.*, Fresenius J. Anal. Chem., vol. 336, 2000, p. 228). In US patent application publication no. 20030016353A1, an approach was proposed based on alternating a burst of shots for ablation and second burst focused in the center

15 of the first burst for sampling. This approach, however, deals with depth profilometry at one position and cannot be applied for scanning the surface.

 The above-mentioned approaches have failed, among others, to eliminate the interaction between the laser and the wall of the crater. Furthermore, these approaches can only be used for one position and for

20 layers in the order of a few micrometers, which is a problem for samples or materials having non-homogenous or heterogeneous compositions due to difficulties in obtaining representative samples.

 Thus, there remains a need for an improved method of removing the coating layer of a sample in order to allow for an accurate analysis of the bulk

25 material realized in real-time using LIBS.

Summary of the Invention

 Briefly, the present invention provides a method and apparatus for preparing the surface of a material for a LIBS measurement.

30 The present invention also provides a method and apparatus for preparing the surface of a material for a LIBS measurement by removing or

ablating the surface coating layer not representative of the bulk material in a very short of time using a special combination of variable duration laser pulses for ablation.

5 There is further provided a method and apparatus for cleaning the surface coating layer by variable pulse duration laser from undesired material not representative of the bulk, preparing that surface for analysis and measuring the evolution of concentration as a function of depth to achieve more accurate measurements than classical instrumentation, without sample preparation.

10 Specifically, the proposed invention is based on a layer-by-layer approach in which a pulsed laser is coupled with high speed scanning optics. To prepare the surface for LIBS, a pulsed laser beam is scanned over an area of the surface to ablate the surface coating layer. Once the surface coating layer is ablated in that area, the laser parameters are changed (i.e. pulse
15 length or duration are made smaller) and the area scanned again to polish the surface. Once the area is polished, the laser parameters are changed again (i.e. pulse duration changed to intermediate pulse duration between the first and second pulse durations) and the area scanned again with spectrometric analysis of the plasma plume created by the laser (i.e. LIBS is performed).

20 More specifically, there is provided a method or process for analyzing bulk material by LIBS, the method or process comprising:

(a) scanning a surface layer of a bulk material to ablate said layer with a pulsed laser beam scanned over the area at a first laser beam regime comprising a first pulse duration;

25 (b) polishing the ablated surface with a pulsed laser beam scanned over the ablated area at a second laser beam regime comprising a second pulse duration shorter than the first pulse duration; and,

(c) scanning the polished surface with a pulsed laser beam within the polished area at a third laser beam regime comprising a third pulse duration of
30 intermediate pulse duration between the first and the second pulse duration to create a plasma plume of the bulk material having optical emissions that are

detected by an optical device. Intermediate pulse duration means that the third pulse duration has a pulse duration smaller than the first pulse duration and larger than the second pulse duration.

The present invention features three different regimes of ablation using the same laser for preparation of the surface of a material. The first regime for cleaning or ablating produces a reproducible and controlled ablation that removes the undesired coating layer at a longer pulse duration (few hundreds of ns), followed by a second regime using pulses of shorter duration (few nanosecond pulses) to polish that surface from any residual coating and giving the material a smooth surface which doesn't lead to repeated oxidation. The third regime for analysis scans inside the cleaned area with overlapped spots in order to avoid the edges of the cleaned area. The third regime probe, collinear with the first, has a smaller sampling area and intermediate pulse duration in between that of the first and second pulse durations to allow generation of low background analytical plasma. The plasma emission is then collected and separated in an optical spectrometer.

The present invention further provides a method of analyzing materials using LIBS, comprising directing a first burst of ablation laser pulses (pulse with hundred of ns) in a first beam at a sample to clean and remove the undesired coating layer and to form an ablation surface according to a pattern with successive overlapped pulses with a bottom and a wall; directing a second burst with shorter laser pulses (few ns), low energy and high repetition rate to remove the residual coating layer, smoothening or polishing the surface and preparing it for the burst of analysis. Directing a third beam with intermediate laser pulses (few tens of ns) in a second beam to scan a smaller width than said first beam at the bottom of said area so as to create a plasma that emits radiation representative of a component in the sample without significant contribution from the wall of the ablation crater, measuring the intensity of radiation from said plasma; determining the concentration of said selected component in said material from the intensity of said radiation; and evaluating the depth at which said plasma is created. The above steps are

preferably repeated in order to determine the evolution of concentration of the selected component as a function of depth.

Many laser systems produce a near-Gaussian energy distribution within the laser beam, which limits the depth resolution achievable with the LIBS
5 technique as it produces cone-shaped craters with a non-negligible peripheral contribution to the ablated mass. The present invention allows one to obtain a more homogenous ablation by using high quality beam distribution. The ablation depth is controlled using a given number of laser shots or laser passes. The invention also allows one to perform an analysis of the surface at
10 the bottom of the ablated zone, without any contribution from the crater wall and at constant fluence on the target allowing for reproducible measurements.

In another aspect of the invention, there is provided an apparatus for depth spectroscopic analysis of a material, comprising:

an energy source for generating pulses of energy in the form of a first
15 laser beam of predetermined pulse duration for ablation of the surface layer of the material;

an energy source for generating pulses of energy in the form of a second laser beam of predetermined pulse duration, said second laser beam having a pulse duration less than said first laser beam; and,

20 an energy source for generating pulses of energy in the form of a third beam of predetermined pulses duration, said third beam having intermediate pulse duration, to form a plasma emitting radiation representative of a selected component present in said material.

In another aspect of this invention, there is provided an apparatus for
25 depth spectroscopic analysis of heterogeneous materials, comprising an energy source for generating pulses of energy in the form of a first beam of predetermined laser pulses duration appropriate for aggressive ablation for removal of undesired materials on a sample by a pattern of several passes with overlapped laser shots to cause ablation thereof and thereby forming a
30 sufficiently large crater with a bottom and a wall; an energy source for generating a burst of pulses in a second beam of laser light, said second beam

having a pulses duration less than said first beam and being directed at the bottom of said crater so as to smooth the surface and remove the residual coating and third beam of laser light with intermediate pulse duration to form a plasma emitting radiation representative of a selected component present in said material without significant contribution from the wall of the crater; a
5 detector for measuring the intensity of radiation of said selected component at different depths of crater; and a depth profile evaluator for determining the depth of the crater for each radiation intensity measurement.

The energy sources can be one, two or three lasers disposed such that
10 their optical paths are substantially collinear. A small deviation from collinearity is acceptable.

The measuring device, e.g. a spectrometer, is preferably disposed substantially collinearly with the optical path of the laser beams.

This invention also enhances the sensitivity and the reproducibility of
15 the LIBS technique by using high repetition long pulse duration laser-induced plasmas with low background continuum.

Further features will be described or will become apparent in the course of the following detailed description. It should be understood that each feature described herein may be utilized in any combination with any one or more of
20 the other described features, and that each feature does not necessarily rely on the presence of another feature except where evident to one of skill in the art.

Brief Description of the Drawings

25 For clearer understanding, preferred embodiments will now be described in detail by way of example, with reference to the accompanying drawings, in which:

FIG. 1 illustrates a schematic diagram of a LIBS apparatus according to an embodiment of the invention.

FIG. 2A illustrates a detail schematic diagram of the ablation regime for cleaning or ablating the surface according to an embodiment of the invention of a layer-by-layer scan pattern.

FIG. 2B illustrates a detail schematic diagram of the ablation regime for polishing the surface for analysis according to an embodiment of the invention of layer-by-layer scan pattern.

FIG. 3 illustrates the ratio of lines intensities of ionized and atomic line of magnesium according to a conventional LIBS (i.e. *site-by-site*) measurement at one position showing the variation of that ratio versus the number of shots on an Avicel/Lactose (1:1 ratio) and 0.5% magnesium stearate tablet, LIBS condition: Fluence: 100 J/cm²; Irradiance: 16 GW/cm², delay 0.5 μs, gate width 2μs, each point are the average of 25 sites and error bar are the corresponding standard deviation for 250 shots per site.

FIG. 4 illustrates the ratio of lines intensities of ionized and atomic line of magnesium versus the successive number of layer using layer-by-layer according to an embodiment of the present invention on an Avicel/Lactose (1:1 ratio) and 0.5% magnesium stearate tablet, LIBS condition: Fluence: 100 J/cm²; Irradiance: 16 GW/cm², delay 0.5 μs, gate width 2μs, each point are the average of 25 shots per layer (i.e. 5x5 close packed spots) and error bar are the corresponding standard deviation for 25 shots per layer for 40 layers.

Fig. 5A Results of a non-gated LIBS experiment at constant average power (20W), 800 ms integration time Aryelle 200 Echelle spectrometer equipped with an Andor Technology DH 334T-18F-E3 ICCD camera, 1 mm circle step 30 μm, scanner speed 200 mm/sec, SPI Laser G3 20 W.

Fig 5B Results of a non-gated LIBS experiment at constant average fluence (11 J/cm²), 1 second integration time Aryelle 200 Echelle spectrometer equipped with an Andor Technology DH 334T-18F-E3 ICCD camera, 1 mm circle step 30 μm, scanner speed 200 mm/sec, SPI Laser G3 20 W.

Fig. 6 Comparison of the evolution aluminium line intensity versus the shot number obtained at the same position (drilling) on steel sample having an oxide layer using conventional laser cleaning with the evolution obtained on

the new 2 step layer-by-layer laser-cleaned surface and by mechanical removal of the oxide layer. Traditional LIBS experiment: 100 mJ on 800 μm (i.e. fluence of 80 J/cm^2 ; irradiance of 11 GW/cm^2) Spectrometer McPherson 2400 grooves/mm; blaze at 300 nm; slit of 30 μm ; plasma image on the slit 1:2.

5 Repetition rate 4 Hz (4 min 10 sec).

Fig. 7 Optical coherence tomography (OCT) images for a) and b) layer-by-layer and c) and d) site-by-site on an 0.5% o-carboxyphenyl phosphate Avicel/Lactose (1:1 ratio) and 0.5% magnesium stearate tablet, with following LIBS conditions: Fluence: 100 J/cm^2 ; Irradiance: 16 GW/cm^2 , delay 0.5 μs ,
10 gate width 2 μs , each point are the average of 25 shots per layer (i.e. 5x5 close packed spots) and error bar are the corresponding standard deviation for 25 shots per layer for 40 layers.

FIG. 8 illustrates a process flow diagram for a method of preparing the surface or ablating according to an embodiment of the present invention. It
15 shows the ablation crater and the plasma formed using a conventional way at a given position and layer by layer according the embodiment of the invention.

FIG. 9 illustrates the result of the first cleaning regime and the second polishing regime leaving a mirror-like surface exempt of undesired material and ready for accurate analysis.

20 Detailed Description of the Embodiments of the Invention

FIG. 1 shows a schematic overview of a LIBS apparatus **100** according to one embodiment of the present invention. The individual components shown in outline or designated by blocks in these figures are all well-known in the LIBS arts, and their specific construction and operation are not critical to the
25 operation or best mode for carrying out the present invention. The apparatus **100** generally includes a pulsed fiber laser **102**, a galvanometer **106**, a high pass filter **112**, a spectrometer **120** and a system computer **140**. The apparatus **100** is configured to generate laser pulses from the fiber pulsed laser **102**. The laser pulses are focused onto a sample **105** with a lens **104** to
30 produce a plasma plume **114** of the sample **105**. The galvanometer scan head **106** is electrically coupled with the system computer **140** for sending a

displacement error signal to automatically correct positioning of the sample **105** during an ablating process as described further below. That galvanometer can be programmed to scan a given surface according to a desired shape on the sample **105**. The apparatus **100** can include a system frame for housing
5 the various components described herein. The system frame can include an air filter for filtering contaminants produced during the ablating process.

The pulsed laser **102** in an exemplary embodiment comprises a fiber pulsed laser for generating energy in the near infrared region of the electromagnetic spectrum with a wavelength of 1064 nm. The pulse duration
10 for the analysis is few tens of ns for generating a laser beam with a power density that can exceed one GW/cm² at a focal point or ablation impact point. The laser **102** can have a repetition rate of approximately 1 MHz or alternately lower than 10 Hz in some embodiments. Alternatively, the pulse duration can vary from few ns to hundreds of nanoseconds. The lens **104** comprises a
15 beam expander and an objective lens used to focus the laser beam on a surface of the sample site **105**. The laser beam can be focused to a spot size of approximately 10-100 micrometers on the sample site **105** according to the desired regime of ablation. In an exemplary embodiment, the laser beam can be focused to a spot size of approximately 150-200 micrometers on the
20 sample site **105**.

A dichroic mirror **112** is used for directing the laser beam toward the sample site **105** and allows reflecting the light emitted by the plasma **114** to be directed to the entrance of optical fiber through the collecting optics **110**. The fiber optic guides the light to a combination spectrometer and detector **120**.

25 The galvanometer **106** allows the beam to scan a desired surface on the target **105** without the need of a complicated stage XY to move the sample. In one embodiment of the invention, the laser beam scans the surface according the pattern shown in Fig 2A for the first ablation regime and for the polishing regime according to the pattern shown in Fig 2B. The horizontal
30 scanning regime is characterized by the scanning speed V_x and horizontal scanning step Δx between two successive laser spots, which are related by

the laser spot size, the scanned surface and the laser repetition rate, e.g. 25 000 Hz. The vertical scanning regime is characterized by the vertical step Δy between two successive lines. The tested scanning regimes are presented graphically in Figures 2A and 2B and representative parameters are given in

5 Table 1.

Table 1: Example of Parameters for Scanning Regimes

Parameters	(1) Ablating/Cleaning	(2) Polishing	(3) Analysis
Pulse duration (ns)	200	9	30
Pulse energy (μJ)	800	40	160
Laser frequency (Hz)	25 000	500 000	50 000
Diameter of the scan (mm)	2	2	1.8
Scan speed (mm/s)	200	7 000	200
Step between spot (μm)	30	30	30
Number of layers	10	2	5

Depending on the speed of the focused beam on the sample, a person skilled in the art will choose a suitable stepping spot. In one embodiment, the galvanometer scan head **106** can have a translation rate of approximately 200

10 mm/s for the first ablation regime and 7000 mm/s for the polishing regime and 200 mm/s for the LIBS analysis.

While the laser beam is focused on the target **105**, the system **120** is collecting the light and monitoring the oxygen line which tags and detects the

15 presence of oxide. Once the oxygen line is not detected or lower than the limit of the detection of oxygen by the detector **130**, the system **140** indicates to the

fiber laser **102** to switch to a shorter pulse duration for polishing the surface and smoothing it from residual oxide or particles from the previous first ablation regime and so on, then the laser beam scans the surface for the third LIBS analysis regime. The third regime devoted to analysis is shown in greater
5 detail in step D of FIG. 8.

The spectrometer **120** in FIG. 1 collects electromagnetic information from the plasma plume **114**. The spectrometer **120** can be monochromator or polychromator. The electromagnetic information includes spectral information identifying an elemental composition of the sample site **105**. A spectral range
10 for the spectrometer **120** can be chosen to suit different applications. In an exemplary embodiment the spectral range can be approximately 25 nm for observing a portion of the electromagnetic wavelength range. Alternatively, the spectrometer **120** can detect electromagnetic radiation in a range of 185 to 930 nm. The light emitted by the plasma plume is directed to the High pass
15 filter **112** through the galvanometer scan head **106** following sufficiently collinear with the light pass for plasma generation. The High pass filter **112** reflects the light to the collecting optics **110** which focus the light to the entrance of fiber cable **124** guiding the light to the spectrometer **120**. The spectrometer **120** reflects the light to a grating that disperses the plasma light.
20 At the exit of the spectrometer **120**, an intensified charge coupled device (ICCD) or detector **130** is coupled with the spectrometer **120** for detecting the dispersed plasma light. The detector **130** provides the detected plasma light to the system computer **140**. The system computer **140** generates spectral information from the emitted plasma light of the laser plume **114**. The spectral
25 information includes intensity data representing elemental information and composition of the sample site **105**. The spectral information can be produced on a display **142**.

The detector **130** provides increased resolution and greater selectivity of the spectral information. The detector **130** includes a micro channel image
30 intensifier plate. The intensifier plate is preferably gated during period of time when the plasma plume **114** emits characteristic atomic emission lines of the

elements. This period coincides with an optimum plume luminance period. This period follows emission of continuum radiation. Continuum radiation lacks useful specific species or elemental information.

In one embodiment, a delay generator (not shown) can be included to provide gating of the detector **130** to allow temporal resolution of the detector **130** response time. Alternative embodiments of the detector **130** can include a detector other than an ICCD, for example a suitable charge coupled device (CCD) or suitable photomultiplier. Accuracy of the spectrometer **120** and detector **130** in one embodiment can generate compositional data in the range of 30 ppm or less. Alternatively, the accuracy can be in the range of a few %. In another embodiment, the accuracy can be in the range of 1%. Also in another embodiment the polychromator can be an Echelle spectrometer or a Pachen Runge spectrometer that can be coupled to several linear CCD covering the whole spectrum 170-900 or some portion of the spectrum of interest depending the application.

The system computer **140** can include application software and a controller in the system computer **140** for providing synchronization of the laser **102**, spectrometer **120**, detector **130**, galvanometer scan head **106**. The galvanometer scan head **106** can be also any kind of optic device to move the laser beam onto the sample. The system computer **140** is electrically coupled with the laser **102**, spectrometer **120**, detector **130**, galvanometer scan head **106** and the detector **130**. The system computer **140** includes a display **142** for displaying spectral information. The system computer **140** can present the spectral data generated on the display **142**. Alternatively, a separate personal computer can also be coupled with the system computer **140** for separately analyzing the spectral information. The system computer **140** can include a power controller to regulate power to all the apparatus **100** components and also sensor for safety.

The application software decodes the spectral information from the detector **130**, facilitates analysis of the spectral information and generates composition information of the sample **105**. The application software allows

setting of certain parameters for performing the laser ablation of the sample site **105**. A spot circle, square or any geometrical shape desired and adapted to the sample **105** can be set as a parameter and can be consistently and precisely maintained through the Galvanometer Head Scan **106** according to the different regime of laser ablation process described in further detail below. Alternatively, according to the application software decoding the information from the detector **130**, a number of passes can be set as a parameter and can be consistently and precisely maintained through the laser ablation process. The spot size of the ablated area decreases depending on the regime of ablation whether for polishing or analysis. Keeping the laser **102** ablated area scanned spot precisely adjusted insures that the sample site **105** produces the plasma plume **114** with consistent optimum plasma plume.

As mentioned above, FIG. 2A shows representative graphical patterns for the first ablation regime. FIG 2A shows the protocol for aggressive ablation and steps A to B of FIG. 8 show the protocol of the second polishing regime for removing the residual undesired material, polishing and preparing the surface for analysis. A spot prepared surface **200** obtained on steel sample by the protocol of the first ablation regime and the second polishing regime according to an embodiment of the present invention is shown on FIG 9.

As mentioned above, for conventional LIBS analysis, the energy distribution within the laser beam (typically a near Gaussian mode in many laser systems) produces cone-shaped craters with non-negligible edge contribution to the ablated mass. The plasma produced by the laser also interacts with the wall of the crater and induces some mixing of material. This complicates the LIBS analysis and causes loss of analytical precision and accuracy, in particular in the interaction with wall of the crater which decreases the fluence on the sample site and affects the emission of the plasma. FIG. 3 shows the evolution of the ionic to atomic magnesium line intensity ratio against the layer number of the site-by-site sampling when using traditional LIBS analysis known in the prior art. The decrease of the ratio due to the decrease of the laser fluence on the target which affects the plasma emission

and the interaction with the wall of the crater (instead of a constant signal) is clear seen. FIG.4 illustrates the evolution of the ratio versus the layer number, specifically, the ionic to atomic magnesium line intensity ratio spectral information shows the stability of the laser-induced plasma temperature when
5 avoiding analyzing the corner or edge of the sampled area. This allows selecting reproducible plasmas to be taken into account in the measurement and it shows clearly an advantage of the approach of the present invention.

Application of this invention is not limited to solid materials and can be used, for e.g, for the analysis of liquids (aqueous and other solutions) where
10 more than a single phase is present, such as high temperature molten materials, for e.g. metals, metallurgical mattes, salts and glasses. This invention is also applicable to the preparation of the surface of materials in liquid phase. This invention can also be used for the analysis of both homogeneous and heterogeneous materials.

15 In the agriculture sector specifically, the invention can be used in various ways to determine the elemental analysis of a soil sample or to determine its PH in order to prepare a fertilization plan. One possibility is to analyse a prepared or non-prepared, heterogeneous or homogeneous, soil sample. These approaches depend on the analysis time available which is
20 limited by the laser frequency. For e..g., it is possible to analyze each sample by using 25000 Hz fiber laser pulses by ablating layer by layer according to the embodiment of the present invention. This allows for an accurate sampling, reproducible measurements and obtaining results much faster than other analytical methods known in the art. The off-line determination by ICP, for e.g.
25 requires sample preparation and analysis that takes one hour or more. Similarly to the analysis of soil, the present invention can be applied to the analysis of metallurgic powder.

In the metal recycling industry, the invention can be used to clean the surface of a metal from paint, fume, dust, oxide etc. and to prepare a clean
30 surface representative of the bulk. By using a high repetition fiber laser rate of 20kHz, one can clean the surface according to the embodiment of the present

invention in less than a fraction of a second and carry out the accurate analysis representative of the bulk. Such analysis can be used for sorting the alloy according to its composition.

What has been described is an improved method and apparatus for
5 preparing the surface of a material for LIBS analysis. The novel features will become apparent to those of skill in the art upon examination of the description. It should be understood, however, that while only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore,
10 to be understood that the appended claims are intended to cover all such modifications and changes and that the scope of the claims should not be limited by the embodiments, but should be given the broadest interpretation consistent with the wording of the claims and the specification as a whole.

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Claims:

1. A method for analyzing bulk material by laser induced breakdown spectroscopy (LIBS), comprising:
 - 5 (a) scanning a surface layer of the bulk material to ablate said layer with a pulsed laser beam scanned over the area at a first laser beam regime comprising a first pulse duration;
 - (b) polishing the ablated surface with a pulsed laser beam scanned over the ablated area at a second laser beam regime comprising a second pulse
10 duration shorter than the first pulse duration; and,
 - (c) scanning the polished surface with a pulsed laser beam within the polished area at a third laser beam regime comprising a third pulse duration of intermediate pulse duration between the first and the second pulse duration,
to create a plasma plume of the bulk material having optical emissions
15 that are detected by an optical device.
2. A method according to claim 1, wherein the ablated surface in step (a) is formed by a pattern of laser passes with successive overlapped pulses.
- 20 3. A method according to claim 2, wherein in step (a), a crater having a bottom and wall is formed.
4. A method according to claim 3, wherein in step (b), the second beam is directed at the bottom of the crater.
- 25 5. A method according to any one of claims 1 to 4, wherein in step (c), the pulsed laser beam scans a smaller area than the pulsed laser beam in step (a).

6. A method according to any one of claims 1 to 5, wherein in step (b), the pulsed laser beam scans a smaller area than the pulsed laser beam in step (a).
- 5 7. A method according to any one of claims 1 to 6, wherein the material is heterogeneous.
8. A method according to any one of claims 1 to 7, further comprising the step of measuring the intensity of radiation from the plasma.
- 10 9. A method according to any one of claims 1 to 8, further comprising the step of measuring the concentration of a component of the material from the intensity of radiation from the plasma.
- 15 10. A method according to any one of claims 1 to 9, further comprising the step of measuring the depth at which the plasma is created.
11. A method according to any one of claims 1 to 10, wherein the optical device is disposed substantially collinearly with the optical path of the laser beams.
- 20 12. An apparatus for depth spectroscopic analysis of a material, comprising:
an energy source for generating pulses of energy in the form of a first laser beam of predetermined pulse duration for ablation of the surface layer of
25 the material;
an energy source for generating pulses of energy in the form of a second laser beam of predetermined pulse duration, said second laser beam having a pulse duration less than said first laser beam; and,
an energy source for generating pulses of energy in the form of a third
30 beam of predetermined pulses duration, said third beam having intermediate pulse duration,

to form a plasma emitting radiation representative of a selected component present in said material.

13. An apparatus according to claim 12, wherein the ablation is conducted
5 using a pattern of laser passes with successive overlapped pulses.

14. An apparatus according to claim 13, wherein a crater with a bottom and a wall is formed by the first laser beam.

10 15. An apparatus according to any one of claims 12 to 14, further comprising a detector for measuring the intensity of radiation of the selected component at different depths of crater.

15 16. An apparatus according to any one of claims 12 and 15, further comprising a depth profile evaluator for determining the depth of the crater for each radiation intensity measurement.

17. An apparatus according to any one of claims 12 to 16, wherein the energy sources can be one, two or three lasers disposed such that their optical
20 paths are substantially collinear.

18. An apparatus according to any one of claims 12 to 17, wherein the pulse duration of the first, second and third laser beams are about 200, 9, and 30 ns respectively.
25

19. An apparatus according to any one of claims 12 to 18, further comprising a delay generator.

20. A method or apparatus according to any one of claims 1 to 19 for use in
30 the analysis of a soil sample.

21. A method or apparatus according to any one of claims 1 to 19 for use in the analysis of a metal sample.

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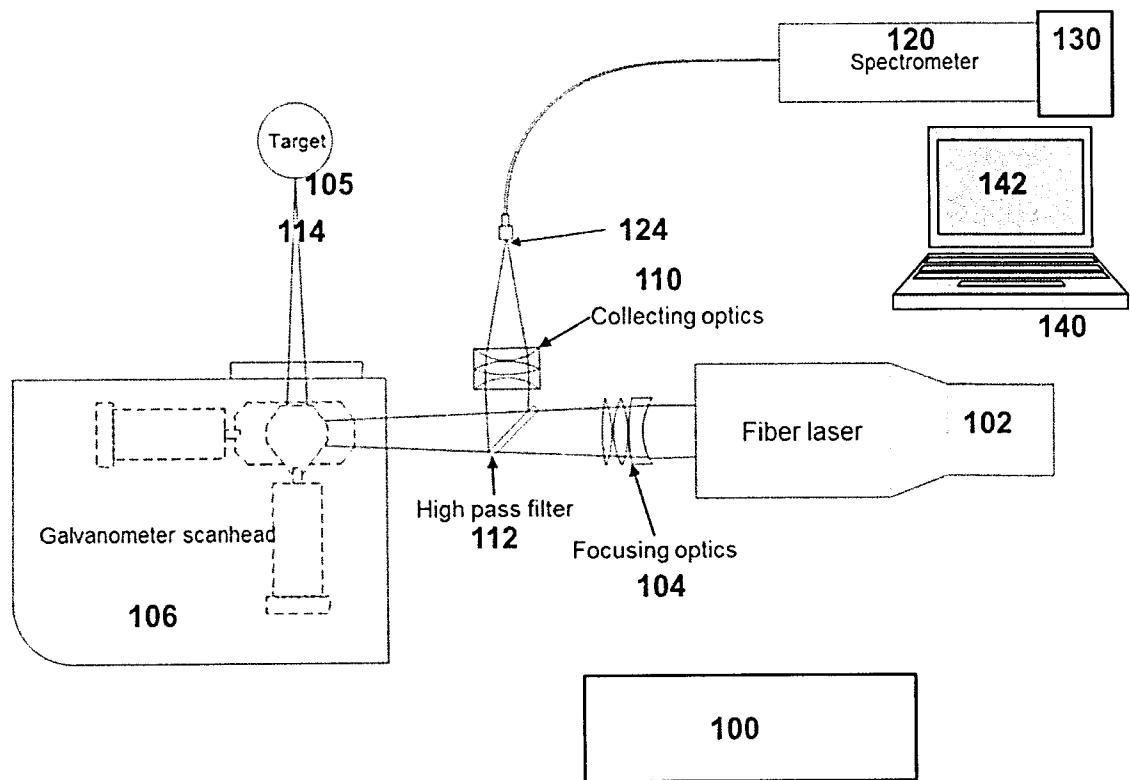


FIG. 1

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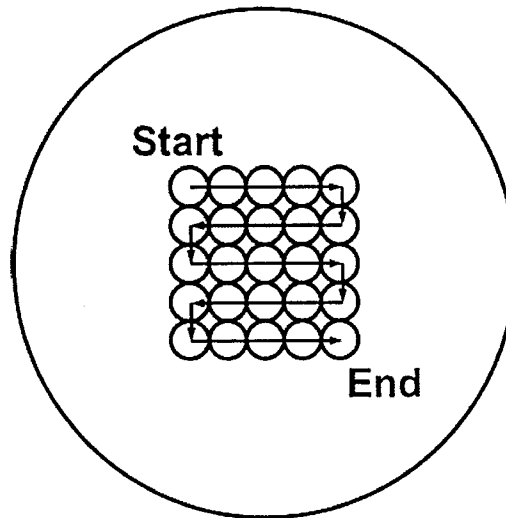


FIG. 2A

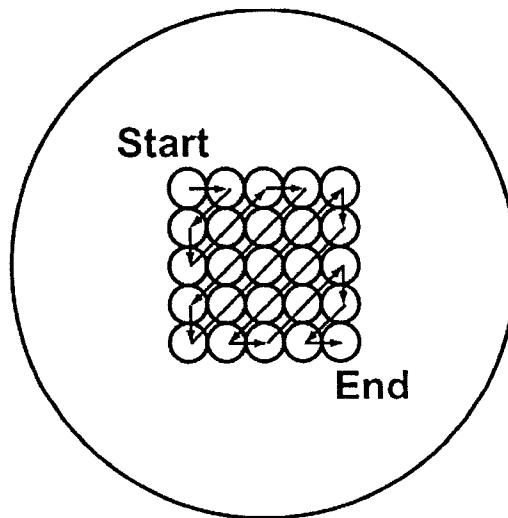


FIG. 2B

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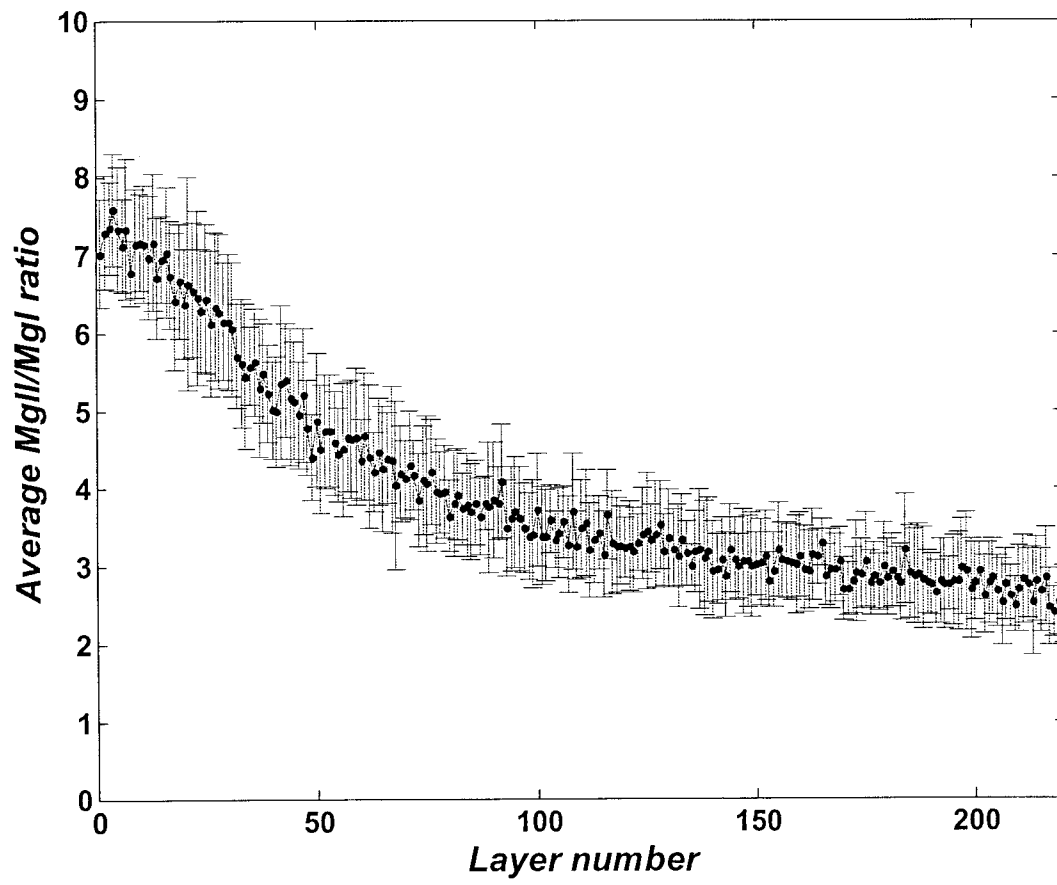


FIG. 3

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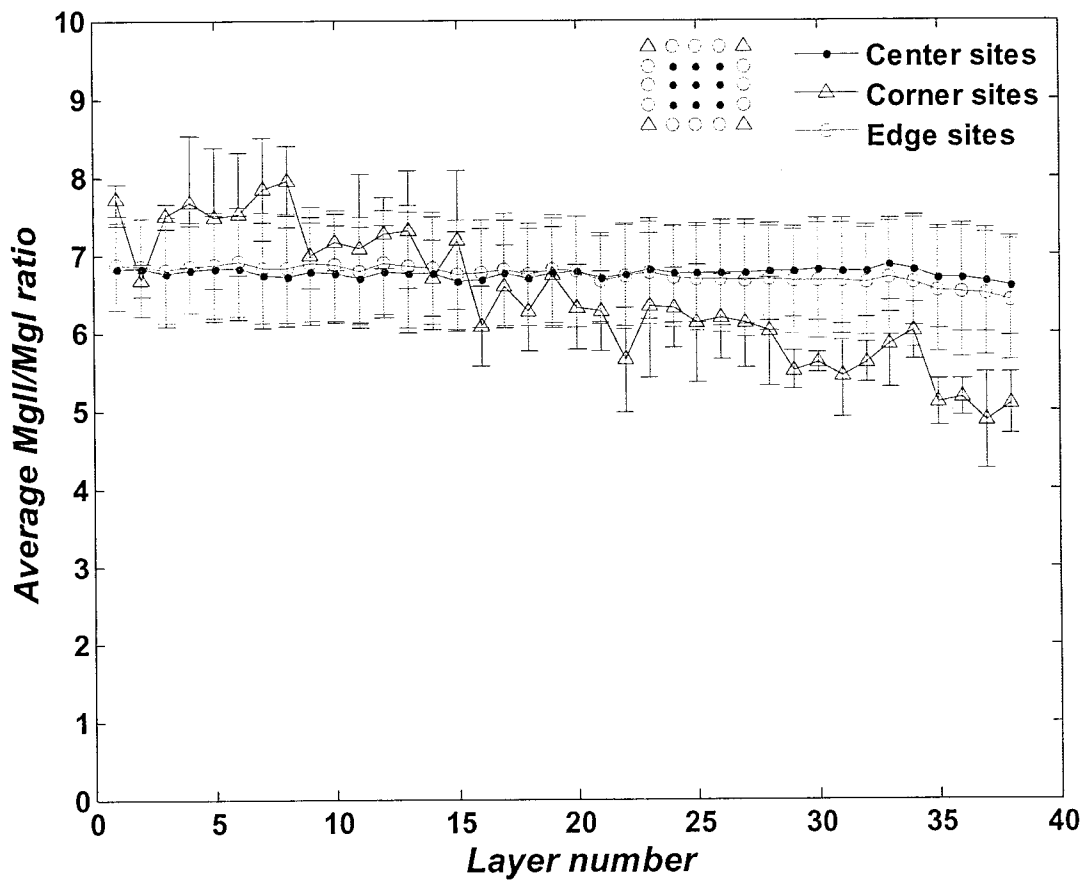


FIG. 4

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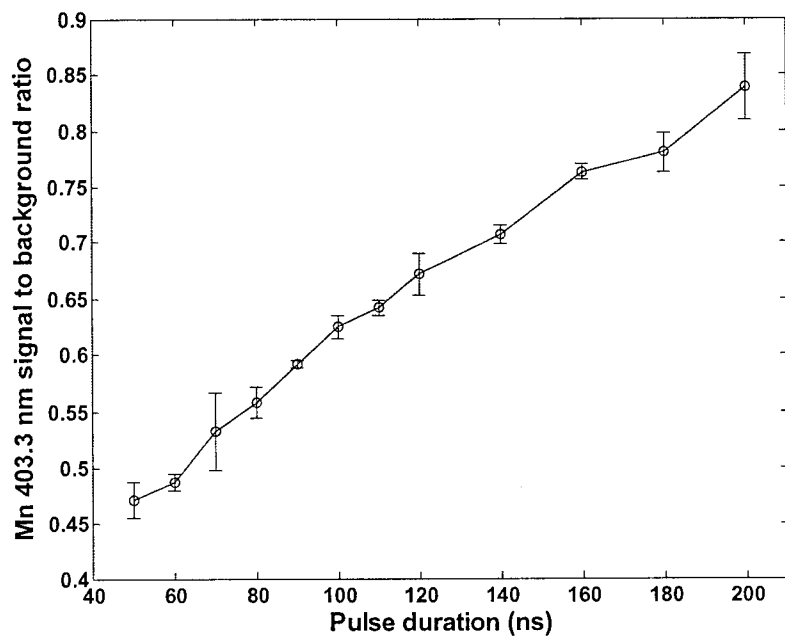


FIG. 5A

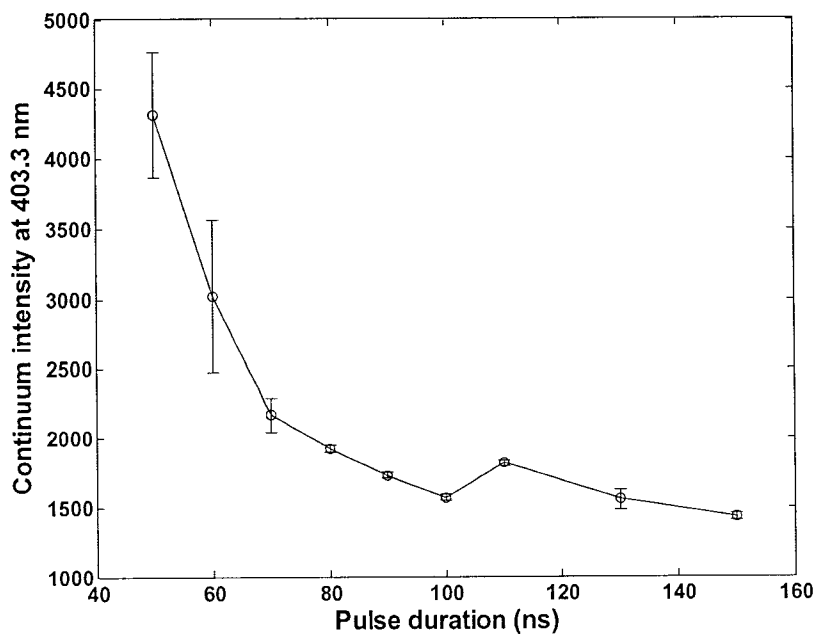


FIG. 5B

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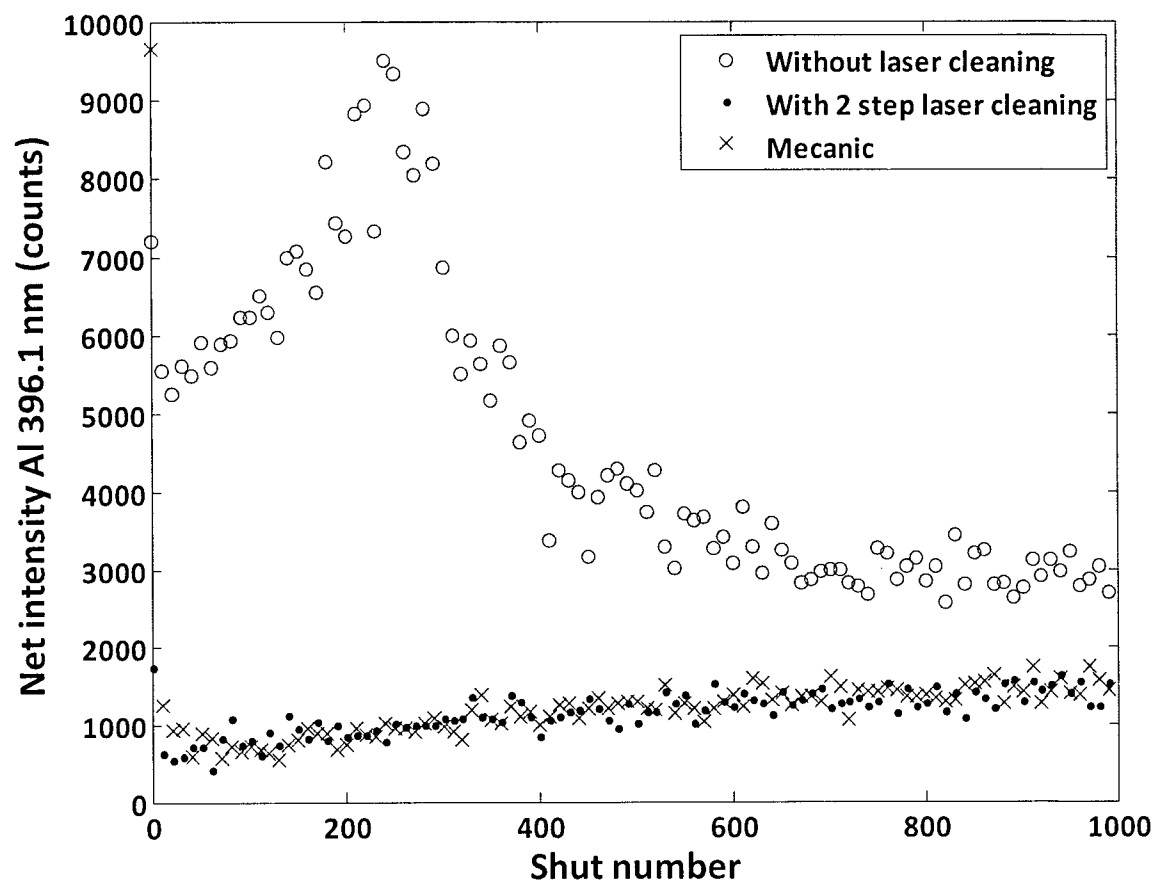


FIG. 6

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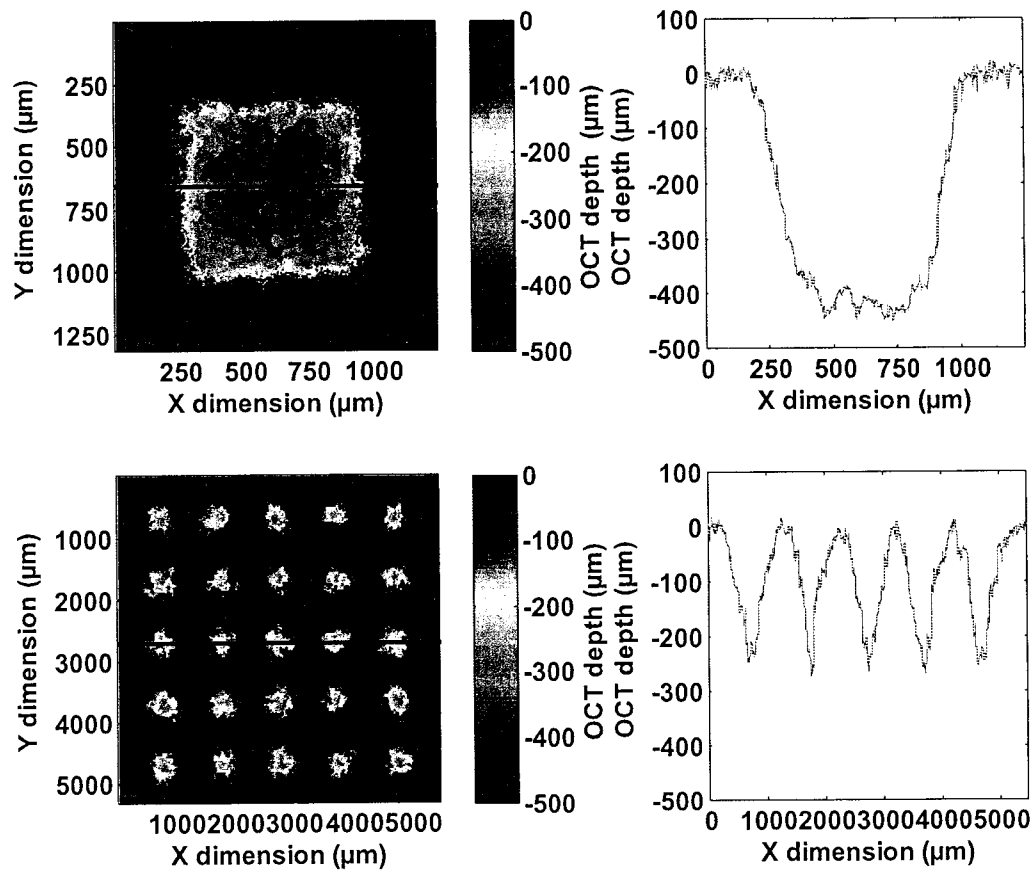


FIG. 7

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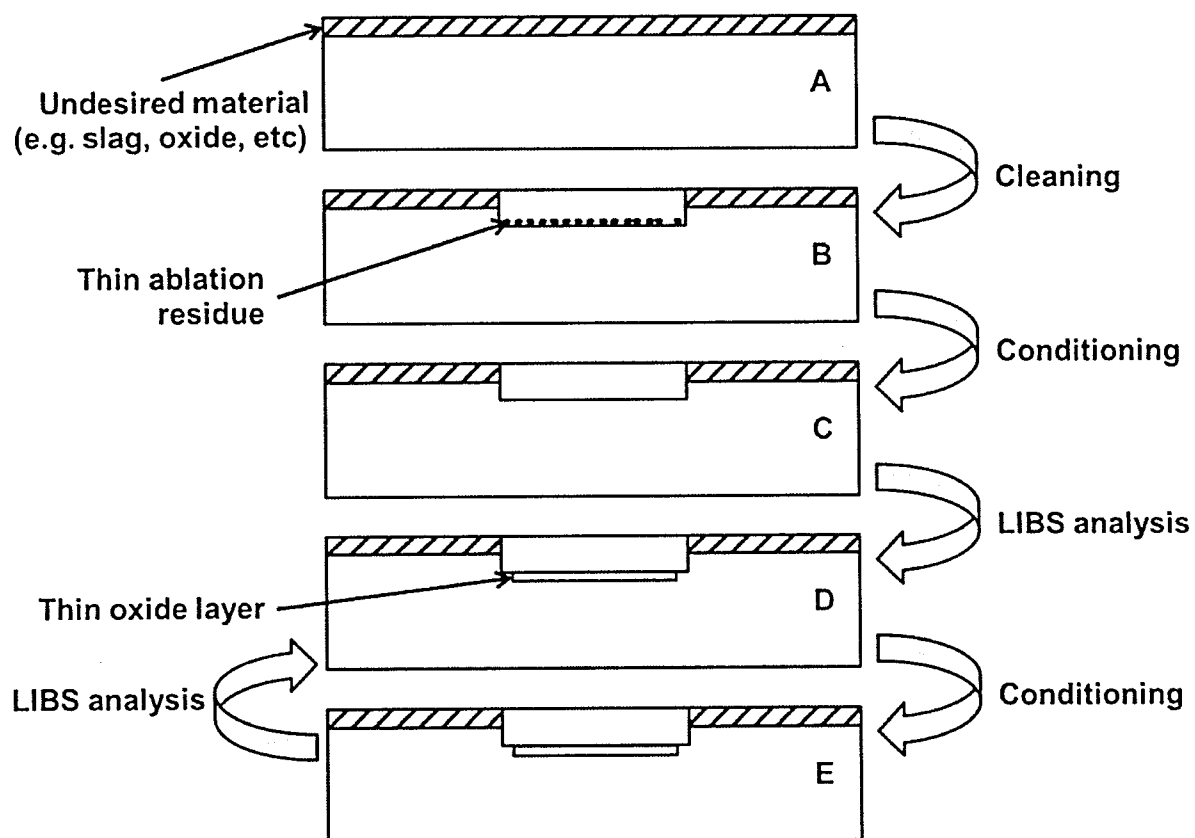


FIG. 8

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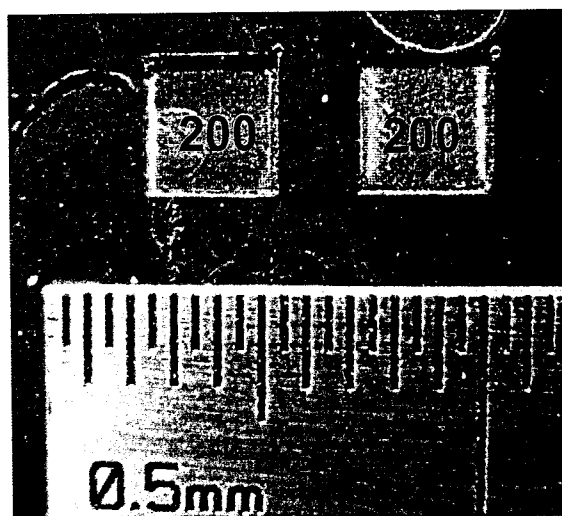


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2014/000850

A. CLASSIFICATION OF SUBJECT MATTER IPC: G01N 21/71 (2006.01), G01J 3/443 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC: G01N 21/71 (2006.01), G01J 3/443 (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Questel and Canadian Patents Database. Keywords: LIBS/ laser induced breakdown spectroscopy, ablation/clean/remove, laser beams, pulse.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6909505 B2 (Lucas et al.) 21 June 2005 (21-06-2005) *Abstract; claims 1 and 20*	1-21
Y	US 2011/0196044 A1 (Hu et al.) 11 August 2011 (11-08-2011) *claims 1, A, 4 and 5*	1-21
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 19 January 2015 (19-01-2015)		Date of mailing of the international search report 12 February 2015 (12-02-2015)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Tariq Khader (819) 934-5149

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CA2014/000850

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
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US2011196044A1	11 August 2011 (11-08-2011)	US2011196044A1 CN102802934A DE112011100502T5 JP2013519671A WO2011100154A1	11 August 2011 (11-08-2011) 28 November 2012 (28-11-2012) 28 March 2013 (28-03-2013) 30 May 2013 (30-05-2013) 18 August 2011 (18-08-2011)