CHEM 517

Fundamentals And Applications Of Laser Induced Breakdown Spectroscopy, LIBS

CHAPTER IV

LASER ABLATION AND ANALYSIS OF SOLIDS BY LIBS

Laser Ablation of Solid Samples:

- **Laser ablation** is the process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam.
- At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates.
- At high laser flux, the material is typically converted to a plasma.
- Usually, laser ablation refers to removing material with a pulsed laser, but it is possible to ablate material with a continuous wave laser beam if the laser intensity is high enough.
- The depth over which the laser energy is absorbed, and thus the amount of material removed by a single laser pulse, depends on the material's optical properties and the laser wavelength.
- Laser pulses can vary over a very wide range of duration (milliseconds to femtoseconds) and fluxes, and can be precisely controlled. This makes laser ablation very valuable for both research and industrial applications.

Laser Ablation (Applications):

- The simplest application of laser ablation is to remove material from a solid surface in a controlled fashion and examples are,
  - pulsed lasers can drill extremely small, deep holes through very hard materials. Very short laser pulses remove material so quickly that the surrounding material absorbs very little heat, so laser drilling can be done on delicate or heat-sensitive materials, including tooth enamel.

Laser Ablation (Applications):

- Also, laser energy can be selectively absorbed by coatings, particularly on metal, so CO_2 or Nd:YAG pulsed lasers can be used to clean surfaces, remove paint or coating, or prepare surfaces for painting without damaging the underlying surface. High power lasers clean a large spot with a single pulse. Lower power lasers use many small pulses which may be scanned across an area. The advantages are:
  - No solvents are used, so it is environmentally friendly and operators are not exposed to chemicals.
  - It is relatively easy to automate, e.g., by using robots.
  - The running costs are lower than dry media or CO_2 ice blasting, although the capital investment costs are much higher
  - The process is gentler than abrasive techniques, e.g. carbon fibres within a composite material are not damaged.
  - Heating of the target is minimal.

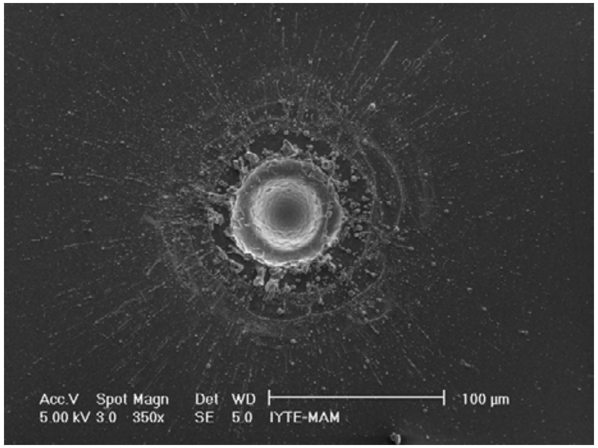
Laser Ablation (Applications):

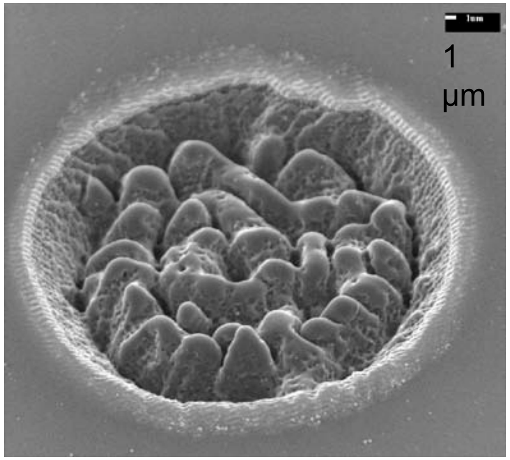
- Another class of applications uses laser ablation to process the material removed into new forms either not possible or difficult to produce by other means. A recent example is the production of carbon nanotubes. Guo et al. (March 1995)[1] were the first to report the use of a laser to ablate a block of pure graphite
- A variation of this type of application is to use laser ablation to create coatings by ablating the coating material from a source and letting it deposit on the surface to be coated; this is a special type of physical vapor deposition, and can create coatings from materials that cannot readily be evaporated any other way. This process is used to manufacture some types of high temperature superconductor.
- Remote laser spectroscopy uses laser ablation to create a plasma from the surface material; the composition of the surface can be determined by analyzing the wavelengths of light emitted by the plasma.

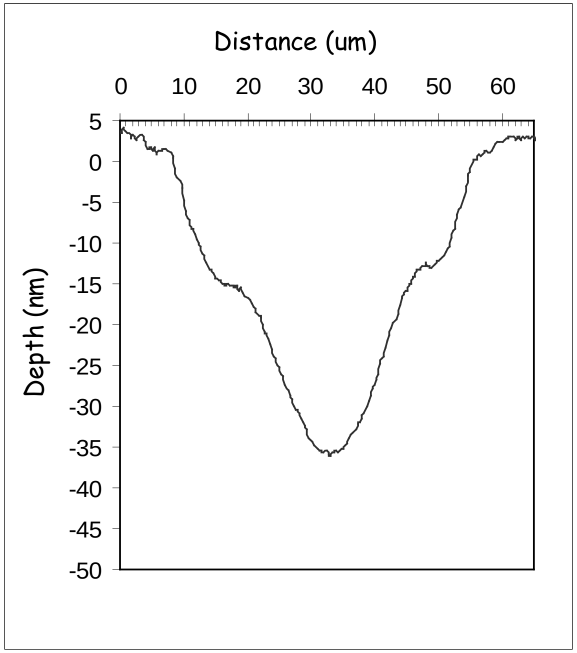
Laser Ablation (Applications):

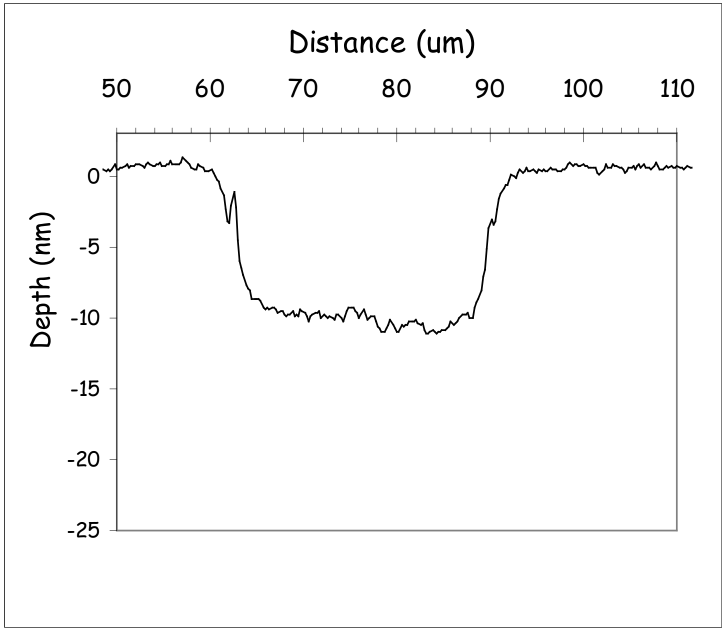
- Finally, laser ablation can be used to transfer momentum to a surface, since the ablated material applies a pulse of high pressure to the surface underneath it as it expands. The effect is similar to hitting the surface with a hammer. This process is used in industry to work-harden metal surfaces, and is one damage mechanism for a laser weapon. It is also the basis of pulsed laser propulsion for spacecraft.
- A Laser ablation has biological applications and can be used to destroy nerves and other tissues. For example, a species of pond snails, Helisoma trivolvis can have their sensory neurons laser ablated off when the snail is still an embryo to prevent use of those nerves

Micromachining-Nanomachining:

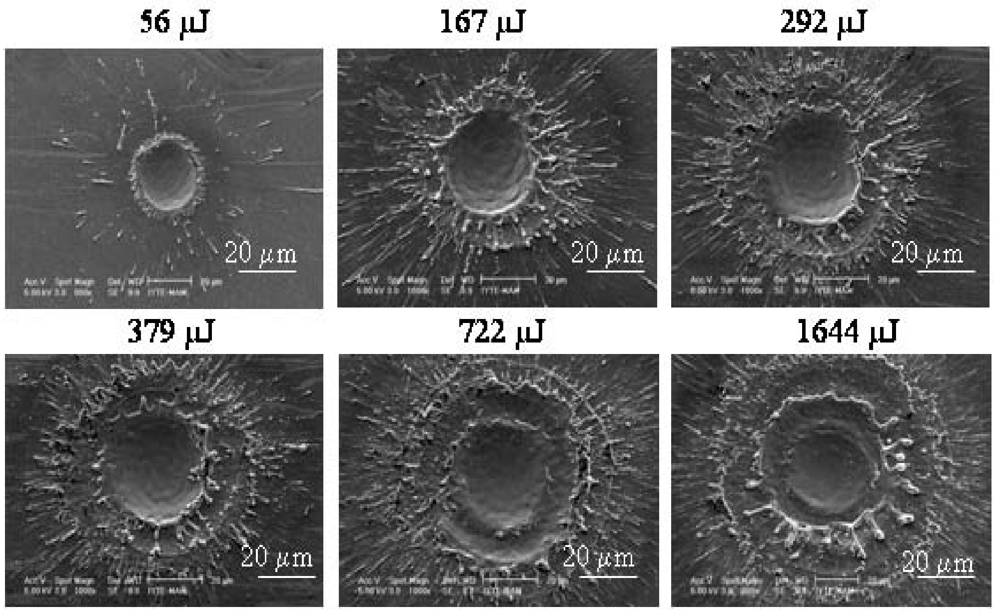








Pulse Energy dependence of the crater size :



$$I_{min} = \rho \cdot L_V \cdot \kappa^{1/2} / \Delta t^{1/2} \left(W/cm^2\right)$$

Moenke-Blankenburg, 1989

ρ = *Density*

L_V = *Latent heat of vap.*

κ = *thermal diffusivity*

Δt = *laser pulse length*

Pure Aluminum: 1.75×10^8 W/cm^2

$GW/cm^2 \Rightarrow$ nanosecond lasers

$TW/cm^2 \Rightarrow$ femtosecond lasers

S. Yalcin, S.Örer, R.Turan, Spectrochimica Acta B, 2008

The diameter of the focused beam size, d,
d =2:44*λ*f/D
λ is the laser wavelength (532 nm),
f is the focal length of the lens (100 mm) and D is the diameter of the collimated laser beam(3 mm, after aperture).

ANALYSIS OF SOLIDS BY LIBS

SURFACE ANALYSIS by LIBS

- Most applications of the LIBS are based on analysis of solid materials.

- Based on the repetition rate of the laser applied, these analyses can be achieved quickly and easily compared to other types of surface analysis techniques.

- LIBS for surface analysis

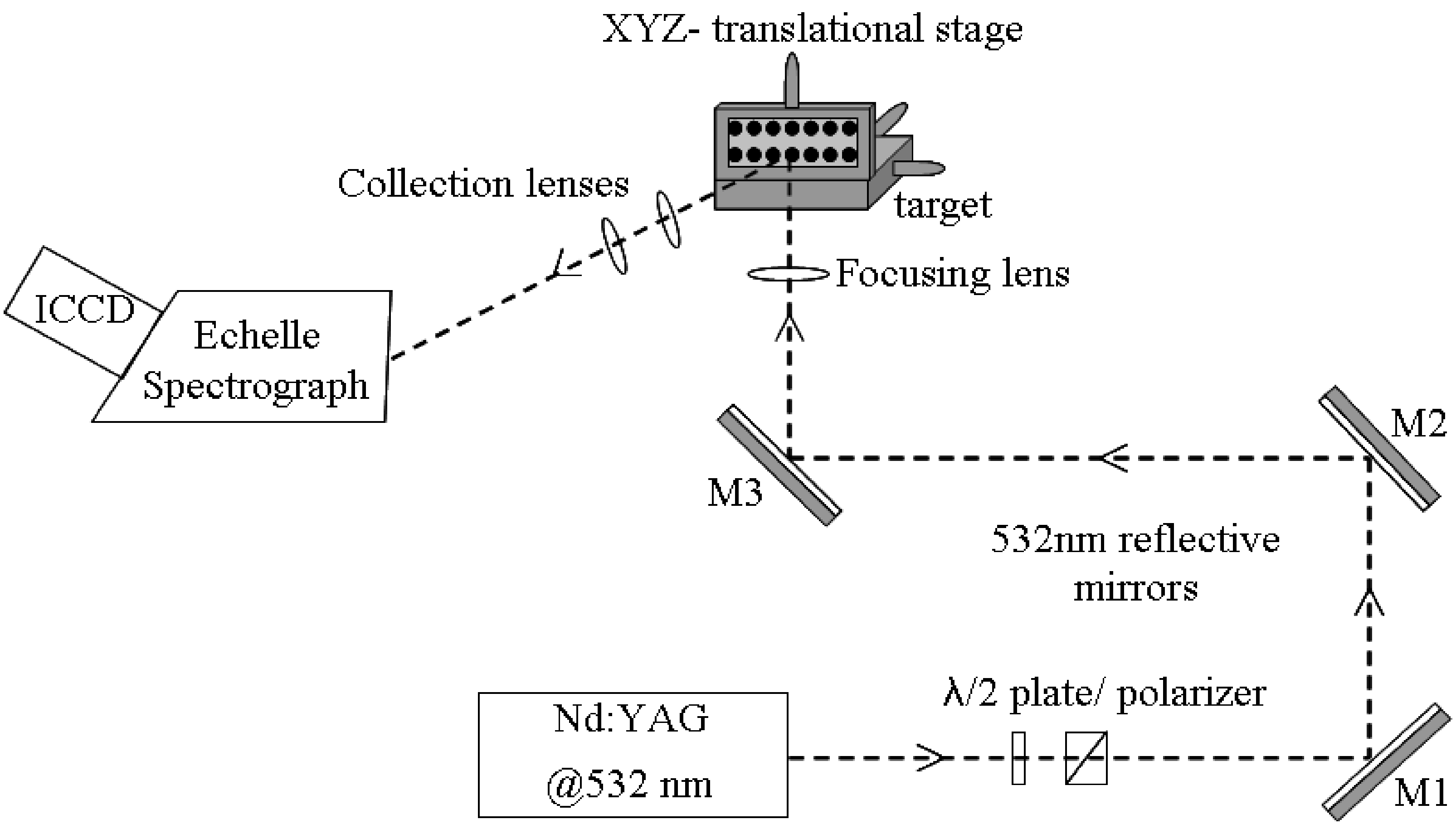
2-D compositional mapping | depth profiling analysis

Two Dimensional (2-D) Compositional Mapping

- LIBS has the capability to confirm the existence of a given element in a precise location → spatial distribution

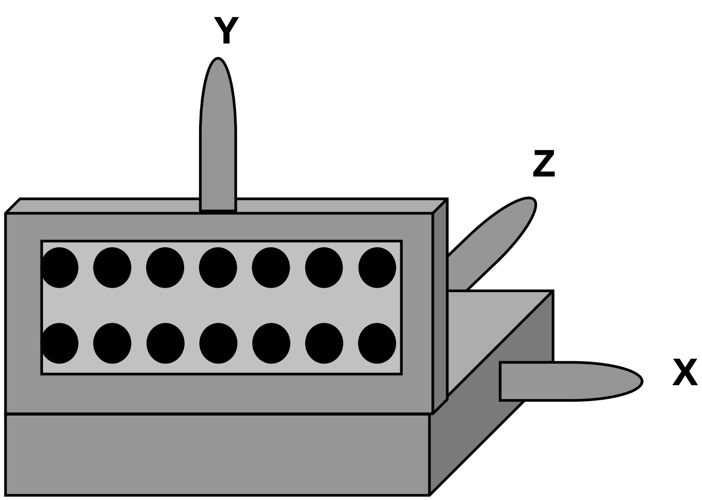
- Spatial distribution of the components gives a simple description of the amount and identity of the material.

LIBS EXPERIMENTAL SET-UP



Two Dimensional (2-D) Compositional Mapping

- Lateral analysis is the acquisition of sequential spectra while the sample moves along a specific path.
- Tight focusing conditions increase the lateral resolution of the measurement



smaller the beam size

↓

better the resolution

<u>crater size;</u>

- energy
- beam size

Two Dimensional (2-D) Compositional Mapping

- *Bette and Noll* (2003) evaluated LIBS for scanning microanalysis up to 1kHz repetition rate.
    - A diode pumped Q-switched Nd: YAG laser was focused on steel samples.
    - A lateral resolution with 20 μm was achieved by a LIBS system.
    - LIBS was proved to be a fast elemental analysis tool in 2-D scanning analysis of surfaces compared to SEM-EDX.

*Bette, H., M.F., Noll, R., **(2003)**. Journal of Physics D: Applied Physics, Vol. 37, pp. 1281–1288.*

Two Dimensional (2-D) Compositional Mapping

- *Taschuk et al.* (2005) was reported a lateral resolution of 10 μm for elemental composition of aluminum alloy surfaces.

  - using 8 μj (266 nm) laser pulses at a repetition rate 5 Hz .

  - Al-Cu-Fe-Mn and Al-Cu-Mg precipitates were found in aluminum alloy by scanning of the surface for compositional mapping.

*Taschuk, M.T., Cravetchi, I.V., Tsui, Y.Y., Fedosejevs, R., **(2005)**.*

Two Dimensional (2-D) Compositional Mapping

- *Cravetchi et.* al employed LIBS to conduct spectrochemical elemental microanalysis of commercially available aluminum alloys in air at atmospheric pressure with Q-SW Nd:YAG at 266 nm.

  - Multi elemental 2-D mapping of precipitate distributions on aluminum alloy sample surfaces was obtained with 10 μm lateral resolution.

*Cravetchi et al, Spectrochim.Acta,Part B, Vol.59, **(2004)**, p.1439*

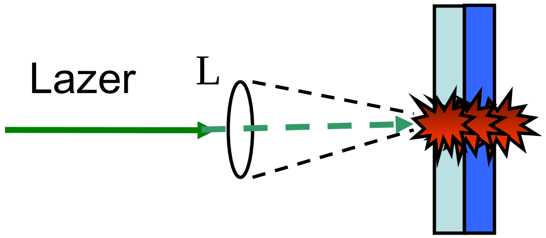
Depth Profiling

- Depth profiling is a method to obtain information on the chemical composition of a sample in a direction perpendicular to the surface.

- LIBS, can be used as a surface and depth analysis method capable of performing direct, fast and easy analysis of any sample regardless of its nature; size and shape, at atmospheric pressure

*Vadillo, J.M. And Laserna, J.J., JAAS, Vol. 12, **(1997)**, p. 859*

Depth Profiling



- Low energy laser pulses sent onto the target surface sequentially to obtain compositional information of the sample in depth.

- Depth resolution is a measure of the thickness of the material ablated
  - laser energy
  - sample type (low mp.)

Depth Profiling

- *Laserna et al.* (1997) analyzed electrically deposited commercial brass samples, which contain a Zn-Cu alloy and different elements with minor percentages.
  - A pulsed Nd: YAG laser (80 mj/pulse, 5 ns pulse duration) at second harmonic level (532 nm) was used to show applicability of LIBS on depth profiling analyses.
  - It was found that ablation rate is at the ng per pulse level and depended on laser irradiance.

Winefordner 2004, Taschuk et al. 2005, Cravetchi et al. 2004

Depth Profiling

- *Milan et al.* (1998) detected depth profiling of phosphorous doping in silicon using Nd: YAG laser at 532 nm.
  - Plasma emission was detected with the charged coupled device (CCD).
  - This study demonstrated the capabilities of LIBS for depth profile analysis of phosphorus doping in silicon.
  - Depth resolution was found to be nearly 1.2 mm.

*Milan et al, App. Spec., Vol.52, **(1998)**, p.444.*

Depth Profiling

- *Ferrero et al.* (2002) tested LIBS as a method for the analysis of Ca in a soil depth profile of Patagonia (Argentina).
    - The use of LIBS in in-situ applications was stated as an advantage for determining total and insoluble Ca in a soil depth profile under optimum experimental operating conditions.

Ferrero et al. ***(2002)****, Spectrochimica Acta Part B, Vol. 57, pp. 303–309.*

Effect of Laser Energy

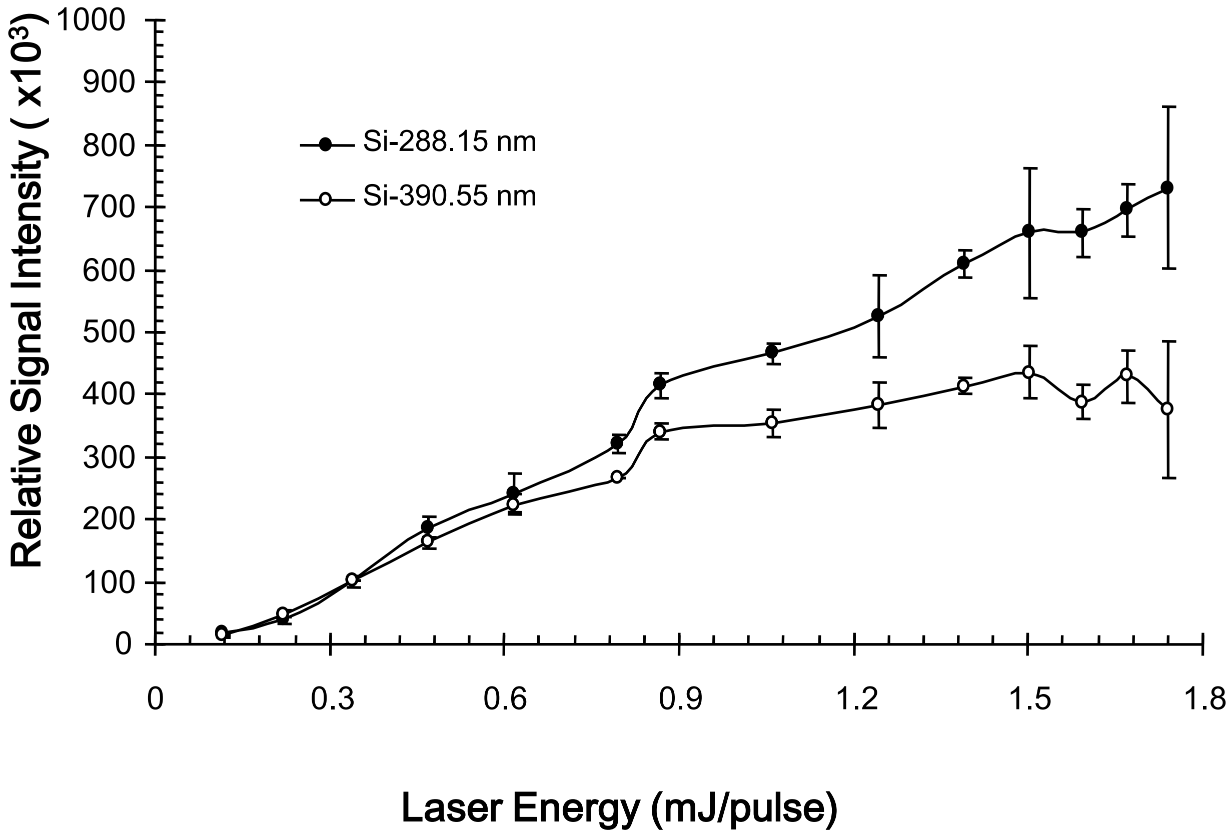
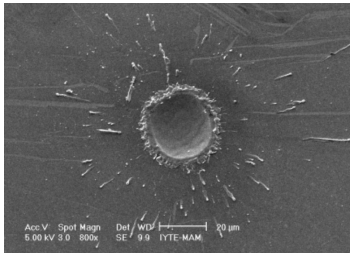
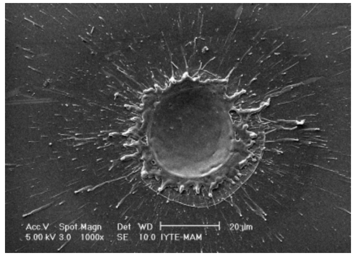


Figure Relative signal intensities of Si–288.15 nm and Si–390.55 nm wrt. different laser energy. The pure silicon wafer has been analyzed with a 10 cm focusing lens and one single laser shot.

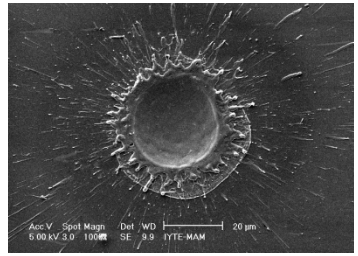
Crater Size;



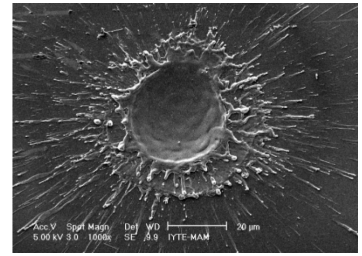
56 mj/pulse



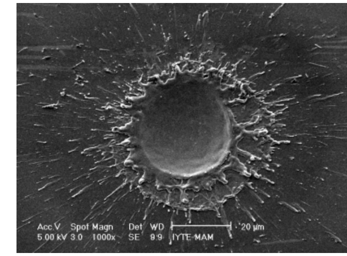
107 mj/pulse



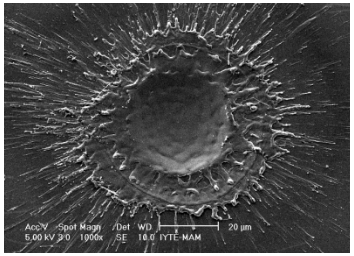
143 mj/pulse



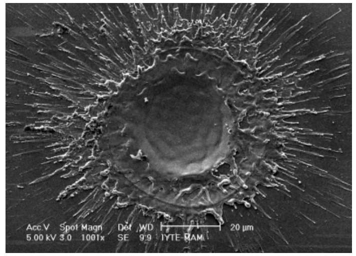
166 mj/pulse



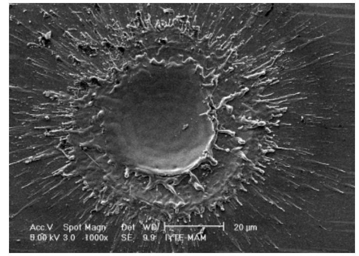
193 mj/pulse



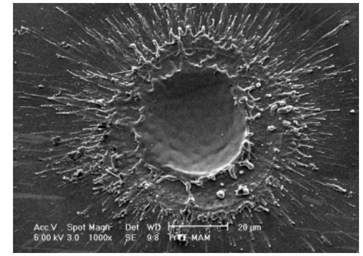
221 mj/pulse



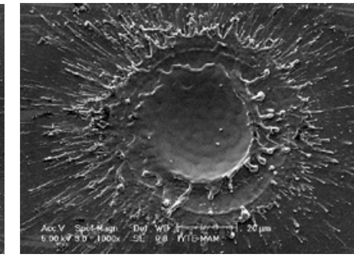
248 mj/pulse



143 mj/pulse



315mj/pulse



351 mj/pulse

<u>Figure</u> SEM images of the craters that were constituted by a single laser shot with 10 cm focusing lens at different laser energies..

Crater Size;

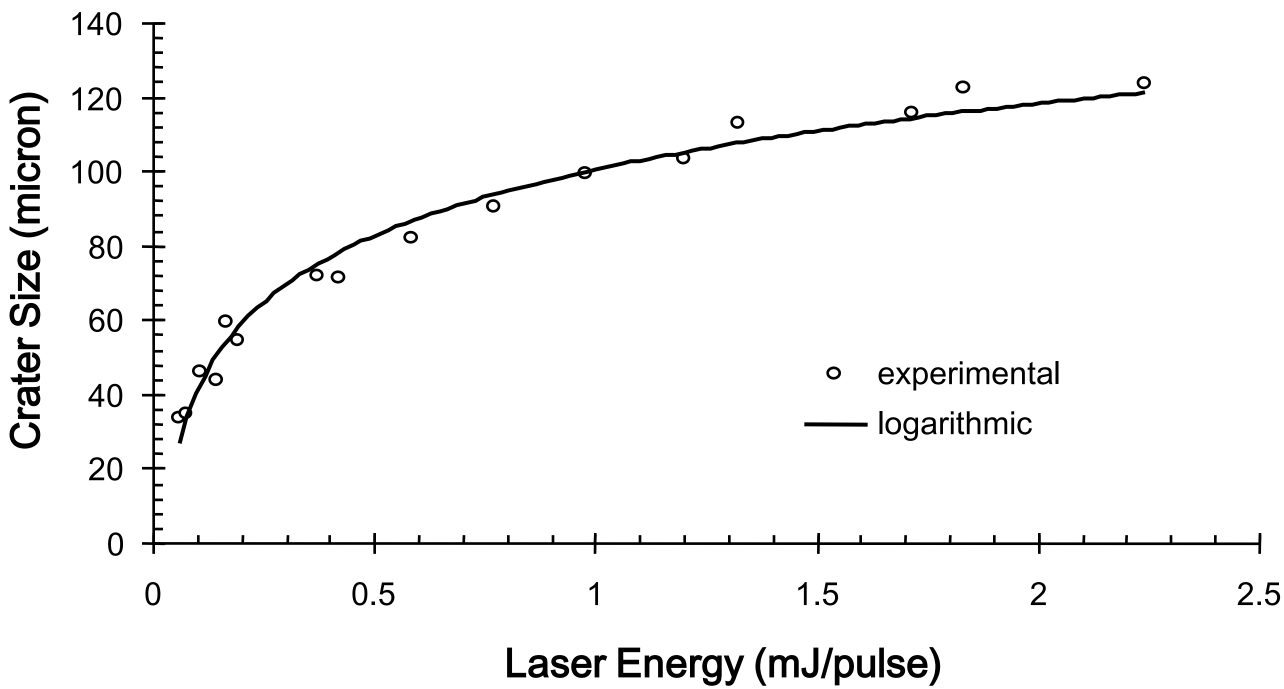
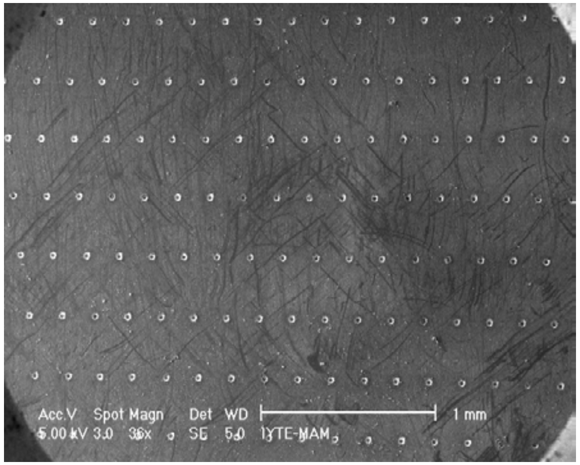
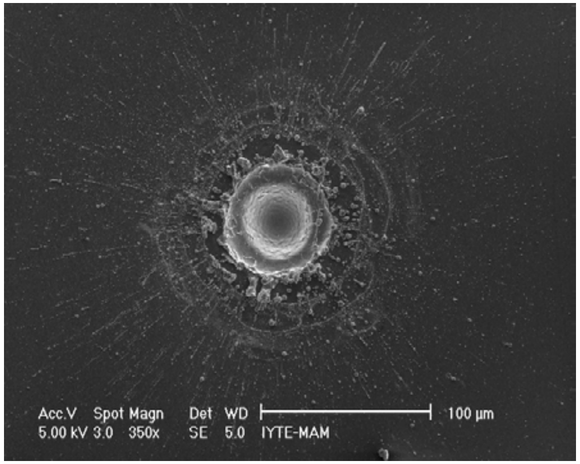


Figure Relationship of laser energy with crater size. The pure silicon wafer has been analyzed with a 10 cm focusing lens and a single laser shot.

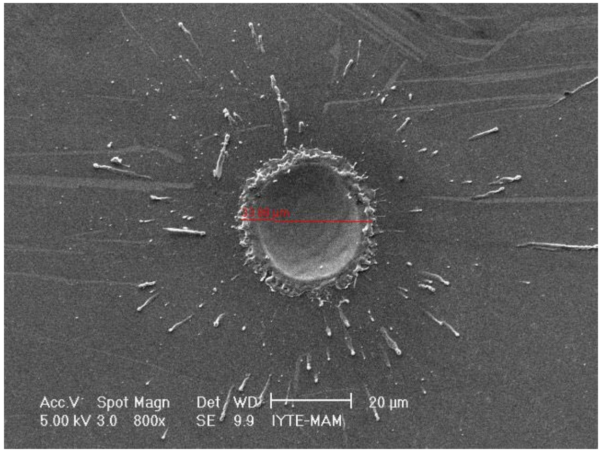
Two Dimensional (2-D) Compositional Mapping



<u>Figure 14:</u> SEM image of the Ge-ion implanted Si wafer within an area of 1.8 x 12 mm^2 . 60 shots has been constructed on each 9 rows with 5 laser shot by a laser energy 250 mj/pulse.



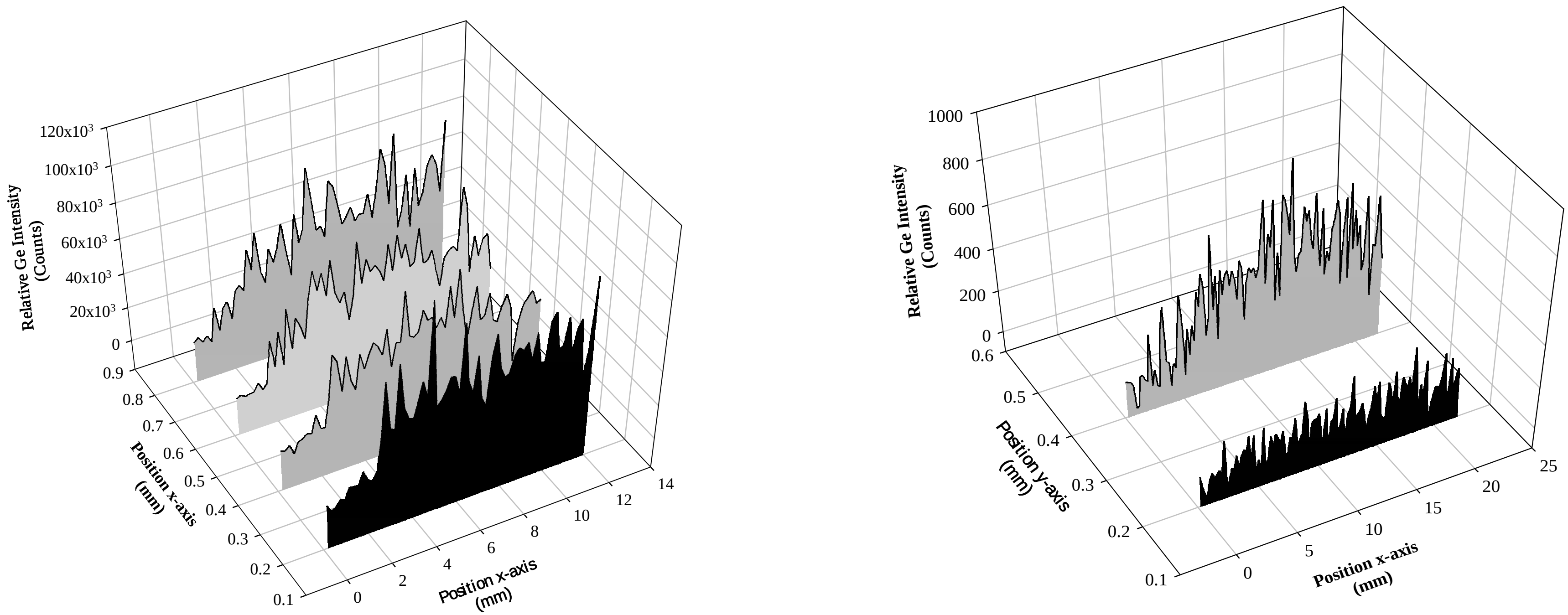
<u>Figure 15:</u> SEM image of the the image of a single crater formed by 5 consecutive laser shots.



<u>Figure 16:</u> SEM image of 33.88 mm crater that has been obtained from a single laser shot of 56 mj laser energy. 10 cm focusing lens is used to focus the laser beam onto a pure silicon wafer.

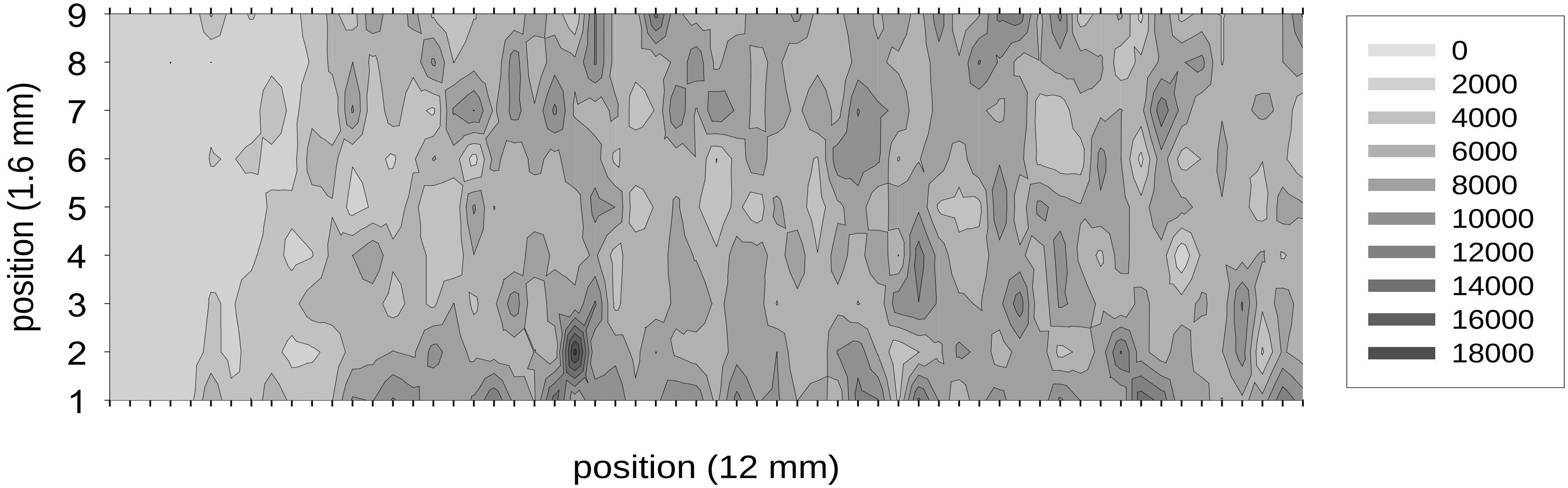
Two Dimensional (2-D) Compositional Mapping

LIBS Analysis;

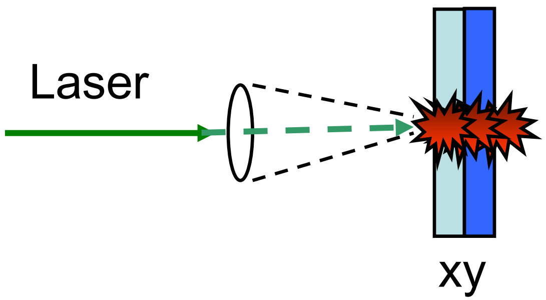


<u>Figure 17</u>: Ge ion distribution on implanted SiO_2 surfaces. (a) 250 microjoule pulse energy, 200 μm sampling intervals in both (x:y) direction, (b) 69 microjoule pulse energy, 50 μm sampling intervals, from implanted region (back) and non-implanted region (front).

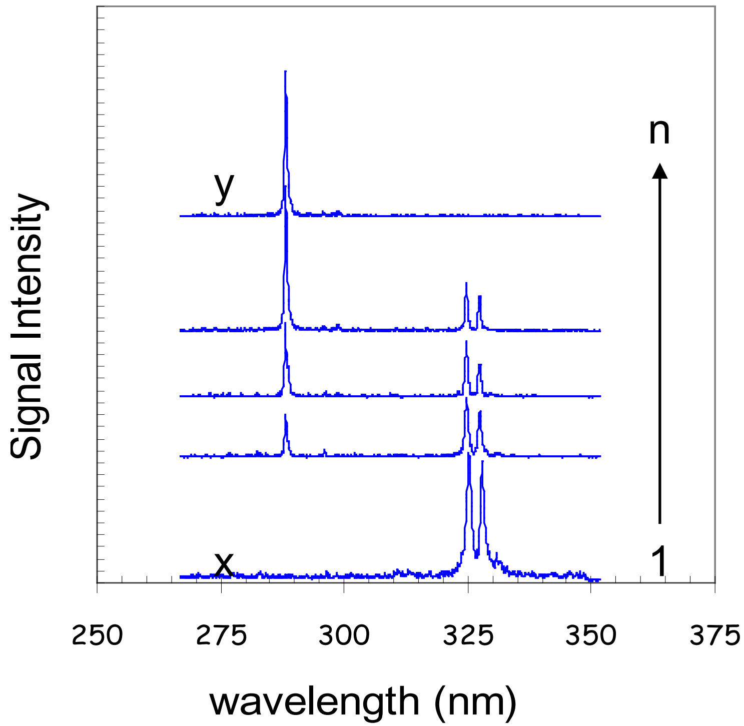
2-D Mapping: Ge ion distribution in Siliconoxide matrix

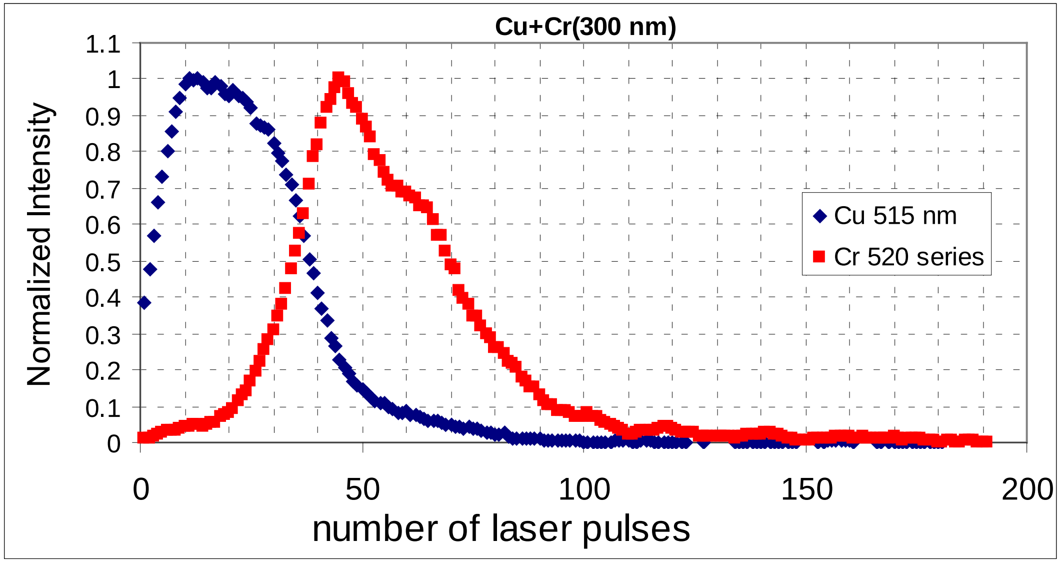


Analysis in 3rd Dimension : Depth Profiling



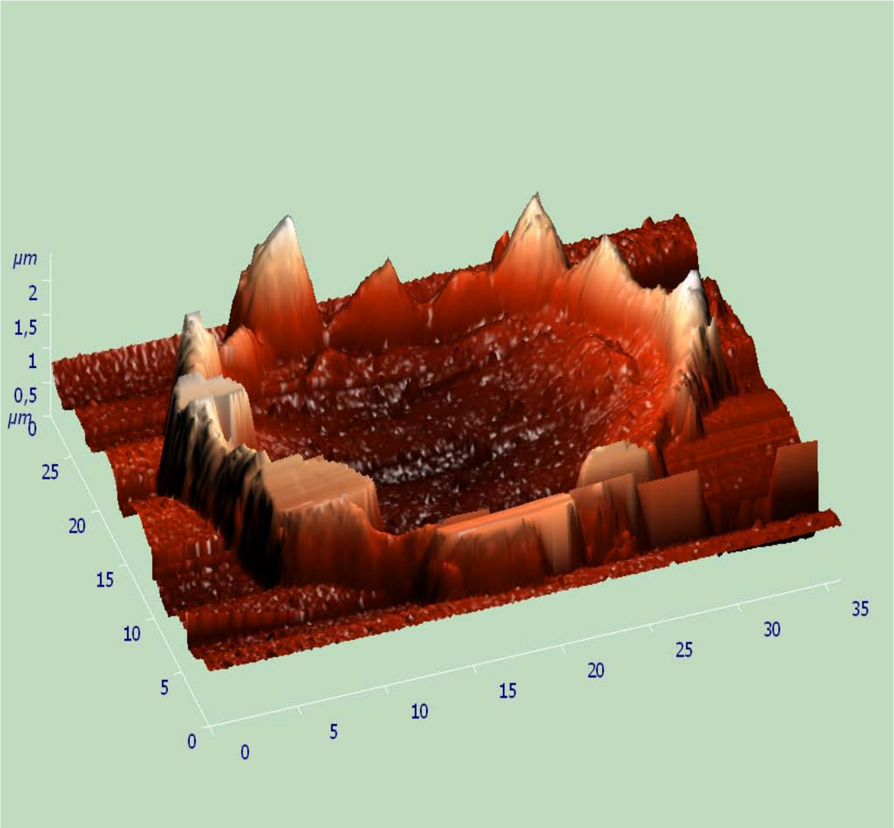
- sequential laser pulses on the same spot
- Multilayer coated samples analysis
- Samples with surface-bulk compositional differences

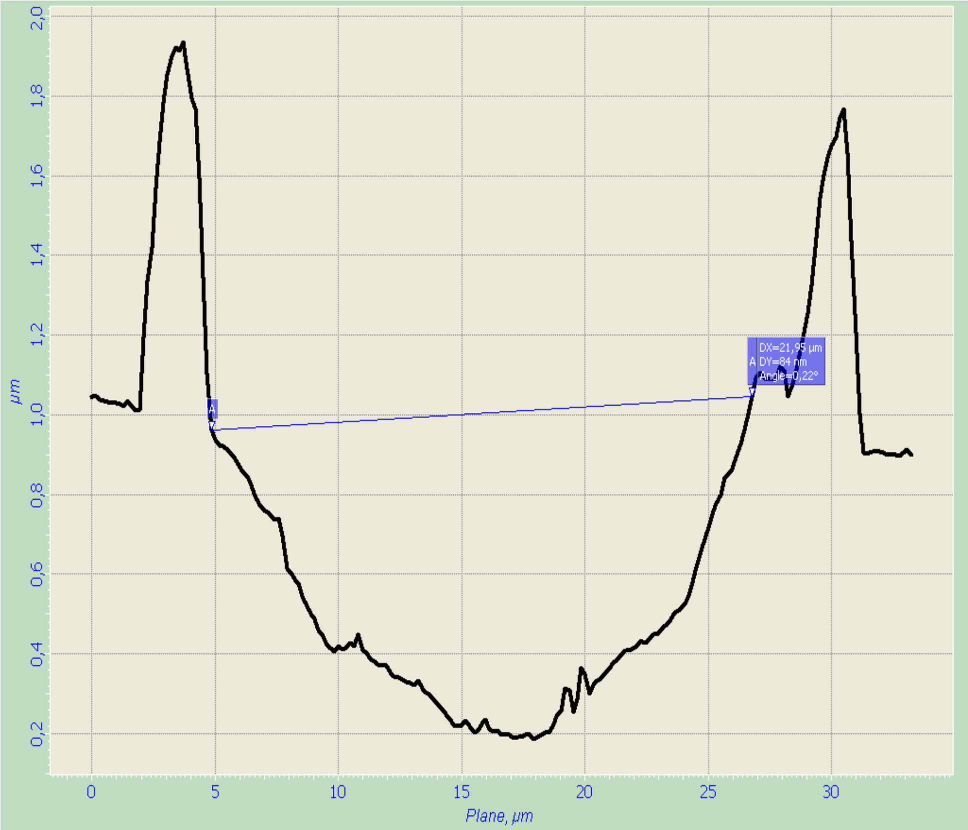




3-D – Depth Analysis:

AFM- Imaging-Si surface





100 µJ/pulse laser energy

Depth:800 nm

Reading Paper Assignment:

ELSEVIER

Spectrochimica Acta Part B 59 (2004) 1439–1450

SPECTROCHIMICA ACTA PART B

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Scanning microanalysis of Al alloys by laser-induced breakdown spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS), using microjoule UV laser pulses, was employed to conduct spectrochemical elemental microanalysis of commercially available aluminum alloys in air at atmospheric pressure. Multi-element 2D compositional mapping with a lateral resolution of about 10 μm in the surface plane of the sample was carried out to measure the precipitate distribution. The elemental composition of features less than 10 μm in size, such as precipitates in the aluminum alloy matrix, was determined by using single 8 μJ laser shots at 266 nm. Two main types of precipitates, namely Al–Cu–Fe–Mn (type I) and Al–Cu–Mg (type II) precipitates, were unambiguously distinguished in our LIBS experiments, in good agreement with electron microprobe X-ray analyzer measurements. It was also observed that the scanning led to the formation of an aluminum oxide layer with a thickness of about 1 μm in the neighboring regions of the laser-scanned area. An additional effect of laser plasma-induced shock wave cleaning of the deposited aluminum oxide layer in a circular region around each laser pulse was also observed. This cleaning effect extends beyond the 10 μm distance to the subsequent laser shot allowing the measurement of the elemental composition of the original surface despite the deposition of an aluminum oxide layer in the surrounding unscanned area.

Keywords: Laser-induced breakdown spectroscopy (LIBS); Multi-element microanalysis; Surface mapping; Aluminum alloys; Shock wave

Reading Paper Assignments:

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Irradiance-dependent depth profiling of layered materials using laser-induced plasma spectrometry

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Laser-induced plasma spectrometry (LIPS) is an appealing technique for depth profiling purposes due to its capabilities for performing fast analysis in air at atmospheric pressure without limitations of sample size or nature. At a fixed laser wavelength, pulse width, experiment geometry and sample type, the irradiance is the factor that will affect both the averaged ablation rate and depth resolution. In the present work, a detailed description of the effect of laser irradiance on averaged ablation rate and depth resolution of Ni–Cu-coated brass samples is presented. The results demonstrate that the best depth resolution does not correspond with the minimum ablation rate. Several facts concerning the redeposition of material around the rim of the craters and energy gradients in the laser beam are proposed to explain the experimental results.