극초단 레이저 생산제조 기술 워크샵

Measurement of material properties and gas flow rates using laser-induced breakdown spectroscopy

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Contents

Pyrotechnic compounds

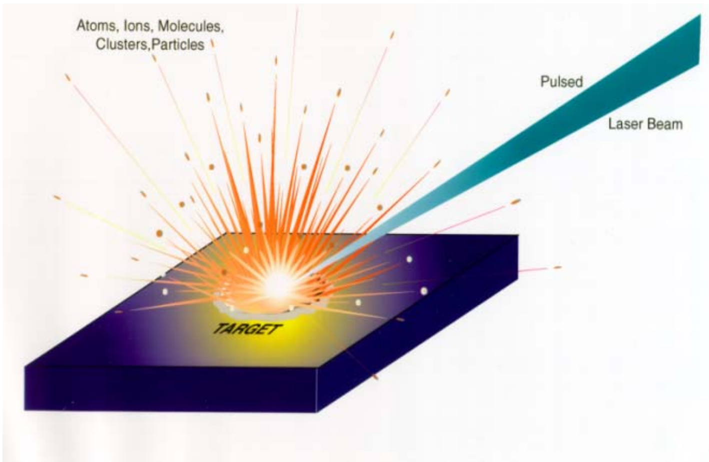
Color	Metal	Example compounds
Red	Strontium (intense red) Lithium (medium red)	$SrCO_3$ (strontium carbonate) Li_2CO_3 (lithium carbonate) LiCl (lithium chloride)
Orange	Calcium	$CaCl_2$ (calcium chloride)
Yellow	Sodium	$NaNO_3$ (sodium nitrate)
Green	Barium	$BaCl_2$ (barium chloride)
Blue	Copper halides	$CuCl_2$ (copper chloride), at low temperature
Indigo	Cesium	$CsNO_3$ (cesium nitrate)
Violet	Potassium Rubidium (violet-red)	KNO_3 (potassium nitrate) $RbNO_3$ (rubidium nitrate)
Gold	Charcoal, iron, or lampblack	
White	Titanium,aluminium, or magnesium powders	

Copper compounds glow green or blue-green in a flame

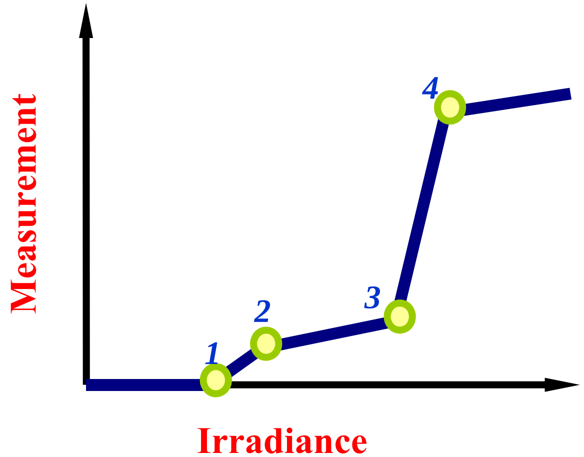
Laser Ablation

Courtesy of **Applied Spectra, Inc. Korea**

Pulse laser beam removes (ablates) a small amount of the sample



Laser Ablation



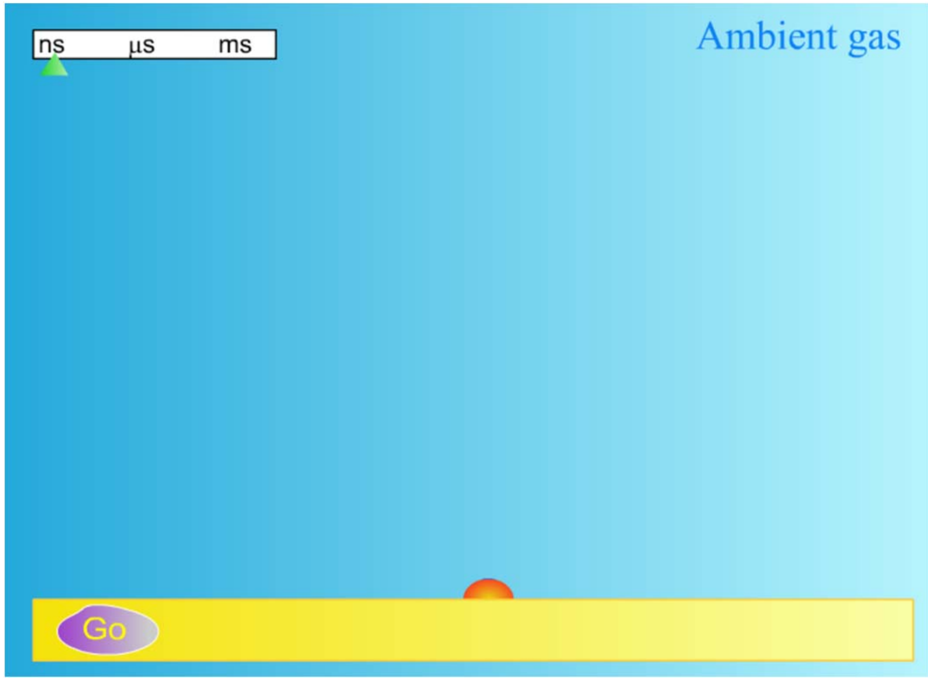
Theory:

Non-linear processes
Laser material interaction
Laser-plasma interaction
Plasma-sample interaction
Vapor phase processes
Vapor phase chemistry

Courtesy of
Applied Spectra, Inc. Korea

Laser Ablation: Shock Processes

- Phenomenological processes (thoughts)



- **ISW = internal shockwave**
  ESW = external shockwave
- **Laser-sample interaction** (~few fs to ~few ns)
- **Vapor plume expansion** (~few ns to ~1µs)
- **Radiative cooling** (~1µs to ~100µs)
- **Vapor plume condensation** (~100µs to ~100ms)

Early Time Plasma Processes and Spectra

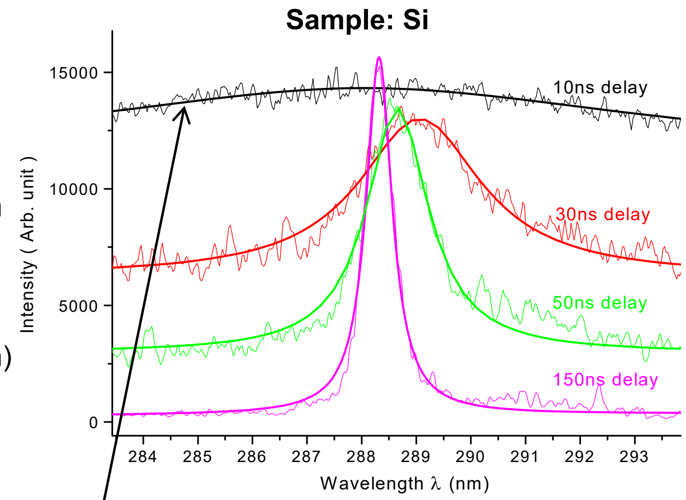
Courtesy of Applied Spectra, Inc. Korea

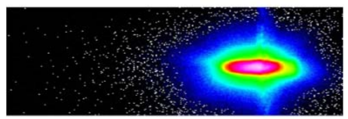
- **Generation of seed free electrons via high power laser pulse**
  - Thermionic emission of electrons from the sample
  - Multi-photon absorption process
- **Free electrons become more energetic and collide with neutral species to generate additional free electrons: cascade ionization.**

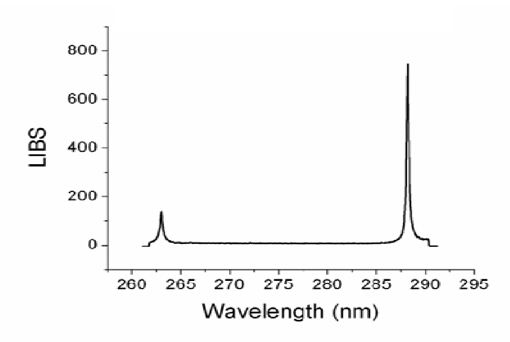
(1) $e^- + h\nu \rightarrow e^{-*}$
(2) $e^{-*} + M \rightarrow M^+ + 2e^-$

(e^{-*} is a more energetic (KE) free electron)

- **More neutral atoms are converted into ions and the temperature (T) and the electron number density (N_e) of the plasma increases.**
- **By the end of the laser pulse, for a typical nanosecond laser pulse**
  - 50%-90% of the laser pulse energy has been coupled into plasma
  - T as high as 50,000K
  - $N_e \sim 10^{18}$ to 10^{19} #/cc
- **Time << μsec: High plasma temperature and electron number density result in *continuum emission*.**
  - Free electron recombination (free-bound)
  - Bremsstrahlung (free-free)
  - Not useful for LIBS analysis



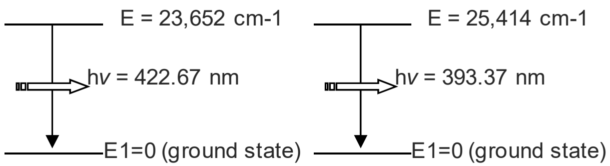




Plasma Cooling and Representative Spectra

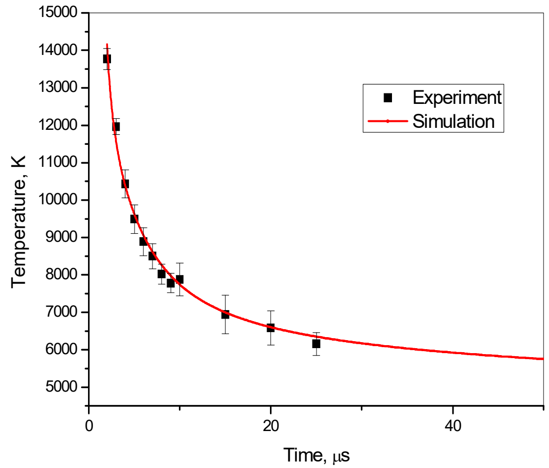
Courtesy of Applied Spectra, Inc. Korea

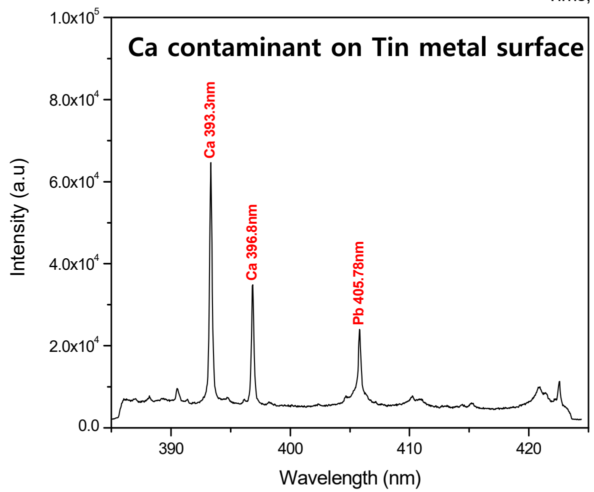
- **~1-30 μs: Plasma temperature and electron number density decrease.**
  - Free electrons become quantized and relax toward electronic ground states, emitting light with distinct atomic/ionic emission lines.
  - Appropriate time window to obtain LIBS signal



Ca(I) – neutral calcium emission **Ca(II) – Ionized calcium emission**

- **Ions and neutral atoms have distinct emission lines.**
- **Atomic emission is proportional to the number of emitting atoms/ions.**
  - Allows for concentration measurements





Gate delay :1 μsec
Gate width: 5 μsec
ICCD gain: 180
Power: 80%
RT100-HP

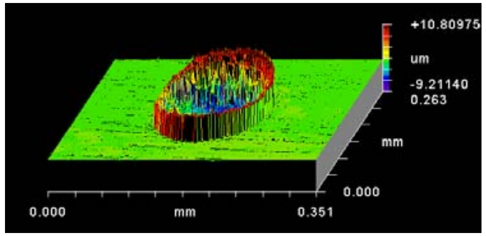
Nanosecond vs femtosecond ablation

Courtesy of Applied Spectra, Inc. Korea

Nanosecond pulse

ns pulsed laser ablation

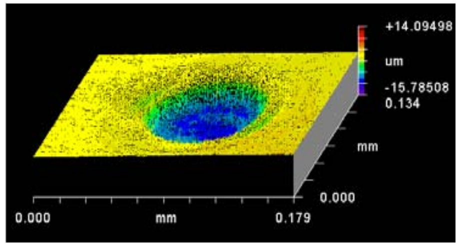
- Large amount of heat in sample
- Melting and vaporization
- Fractionation
- Ejection of large melted particles



Femtosecond pulse

fs pulsed laser ablation

- Very little heating and melting
- Photophysical explosion
- No fractionation
- Condensation of nano-particles



fs laser ablation more accurate, precise, efficient!
Offers more capabilities (high rep rate)

LIBS Process

Courtesy of
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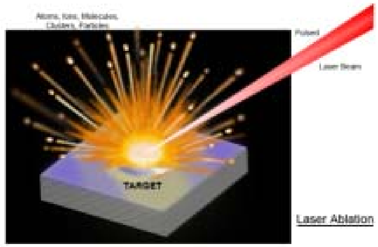
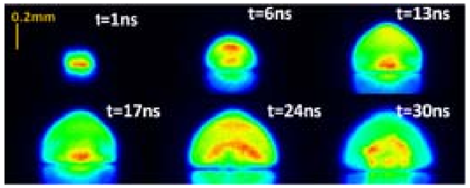
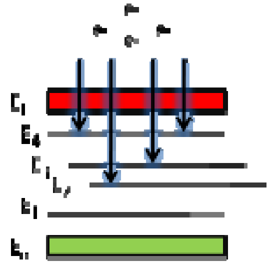


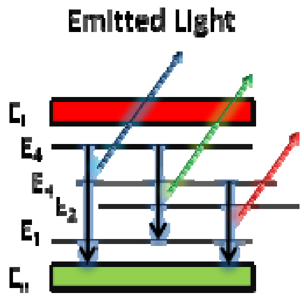
Laser Ablation for LIBS:
Focused laser beam to generate a tiny, short-lived plasma



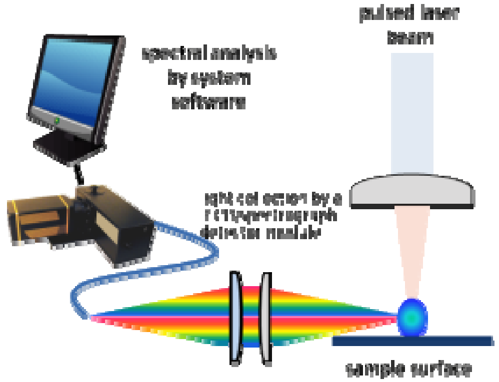
Initiation of a high temperature plasma and its expansion above the sample surface



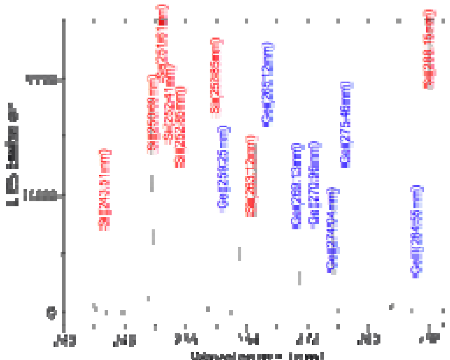
Continuum emission during early stage (< 200 ~ 300 nsec) of plasma cooling process (white light and not useful)



Discrete atomic line emission at later times (> 1 μsec) (useful for analysis)



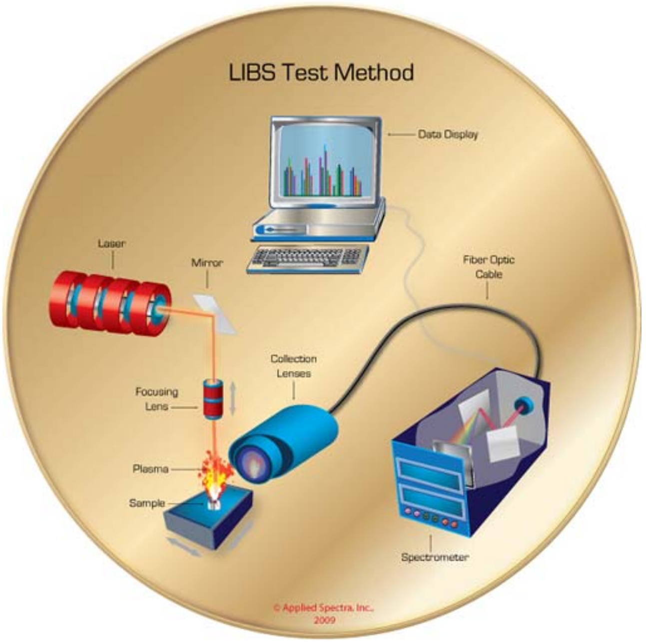
Emitted light collection by a set of optical lenses and optical fiber



Display of LIBS spectra and their subsequent analysis by system software for both qualitative and quantitative elemental analysis

Setup for LIBS

Courtesy of Applied Spectra, Inc. Korea



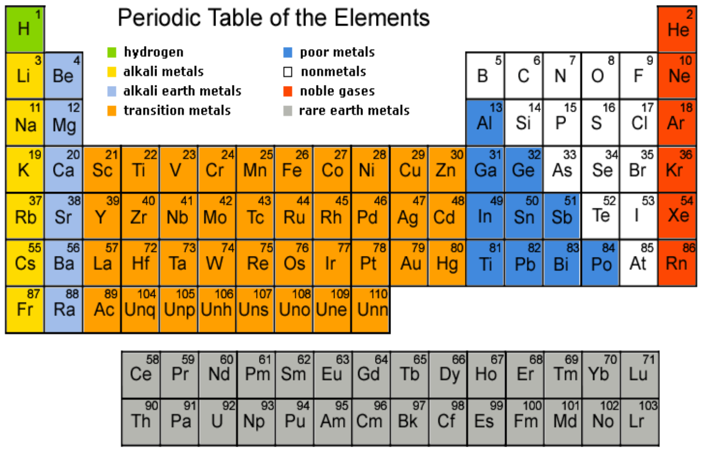
LIBS uses laser ablation plasma to analyze emission spectra for both qualitative and qu antitative analysis of elements.

- Laser
  - Its Beam is focused onto the sample to create a tiny plasma
- Focusing and collection optics
  - Optics to deliver the laser beam to the sample and to collect the light from the plasma
- Spectrometer and detector camera
  - Disperses the collected light and separates the emission peaks for elemental analysis
- Sample stage
  - Specifies particular locations for the analysis and allows set-up of appropriate sampling protocol
- Computer system
  - Data collection and analysis
  - Controls the precise timing of the plasma emission analysis

LIBS Advantage

Courtesy of
Applied
Spectra, Inc.
Korea

- **Can analyze virtually all elements in the periodic table**
  - High sensitivity for low lighter elements that include Li, Be, B, C, Na, and Mg (~ ppm level)
  - Ability to measure organic elements such as O, H, and N
  - Ideal for analysis of transition metal impurity (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Hf, W, Mo, Zr, Ag, Cd, etc) (~ 10's of ppm level)
- **Measurements commonly done in air (no vacuum)**
- **A fast measurement time**
  - A short plasma lifetime lasting only a few tens of μsec
  - A few seconds per measurement
- **Flexible sampling protocol**
  - Bulk analysis
  - Depth profiling
  - Elemental mapping of sample area
  - Inclusion analysis
- **High detection sensitivity for even small and thin samples**
  - No interference from underlying layers

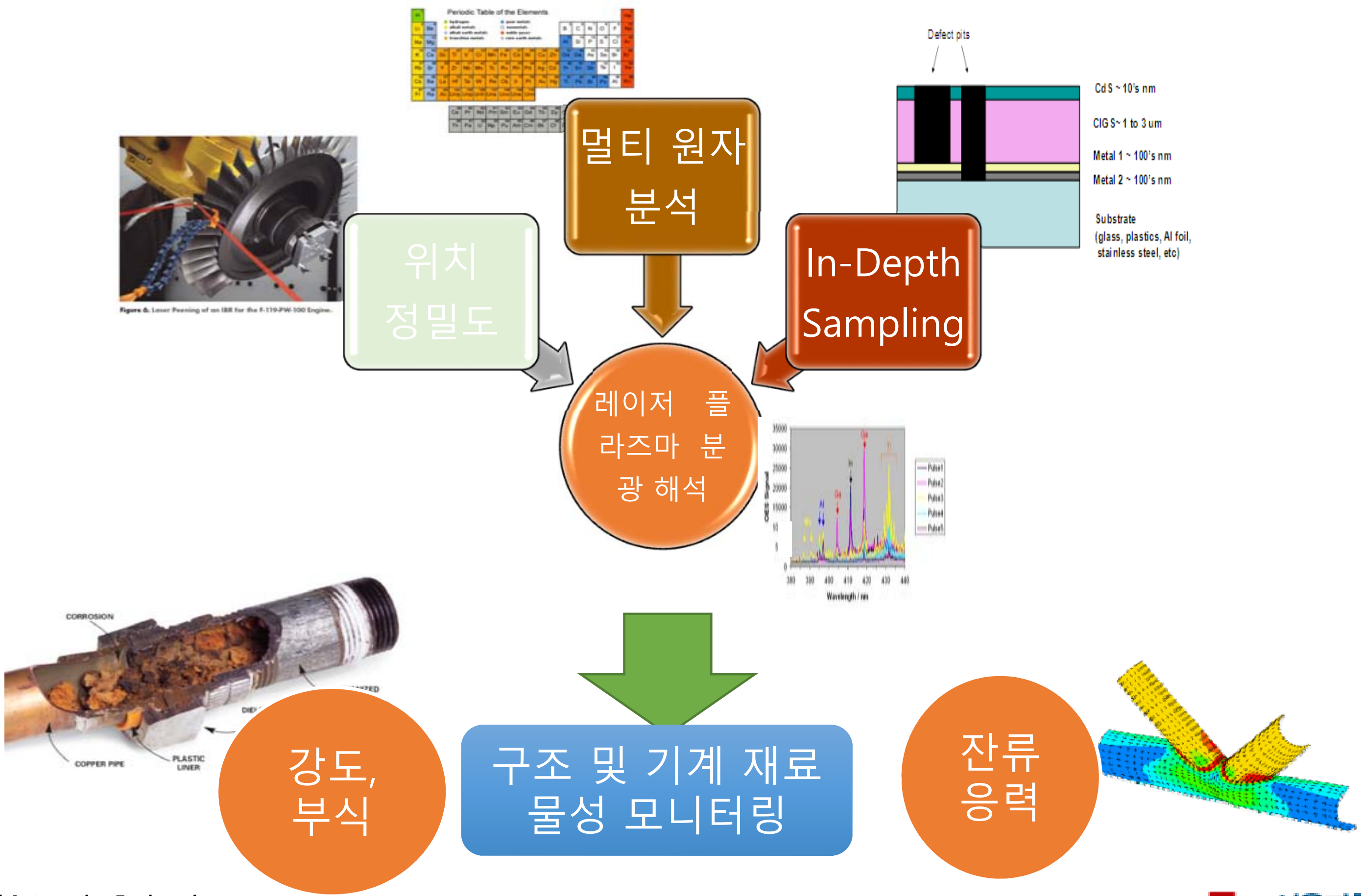


Comparing existing measurement techniques to laser induced plasma spectrometry

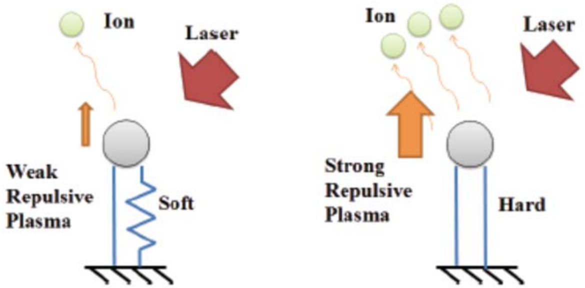
Courtesy of Applied Spectra, Inc. Korea

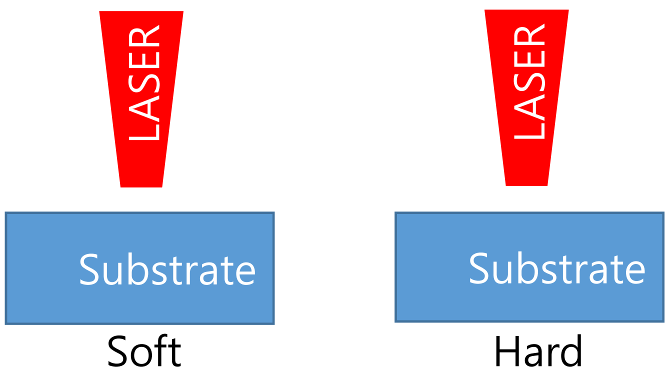
LIBS	SEM-EDS	XRD	ICP-MS
정성 분석 가능	정성,정량분석 가능	정량분석이 힘듦	정성, 정량분석 가능
모든 시료 분석가능	액체,기체 분석불가	액체, 기체, 비정질재료 분석 불가	모든 시료 분석가능
대기상태분석가능	대기상태분석불가	대기상태분석불가	대기상태분석불가
심도 분석 가능	심도 분석 불가	심도 분석 불가	심도 분석 불가
시료 전처리 과정 없음	시료 전처리 과정 필요	시료 전처리 과정 필요	시료 전처리 과정 필요
실시간 모니터링 가능	비 실시간 장치	실시간 모니터링 가능	비 실시간 장치
ppm단위 분석 가능	0.1wt.%	0.1wt.%	ppb단위 분석 가능

LIBS Applications



Measurement of surface hardness by LIBS



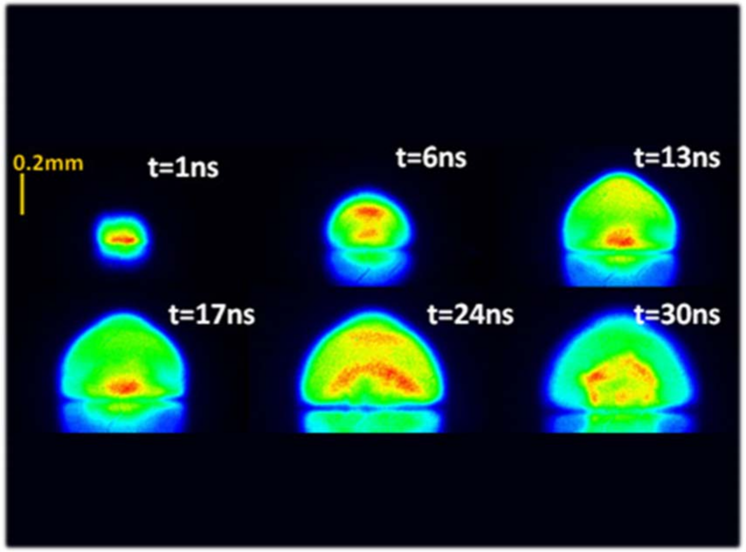


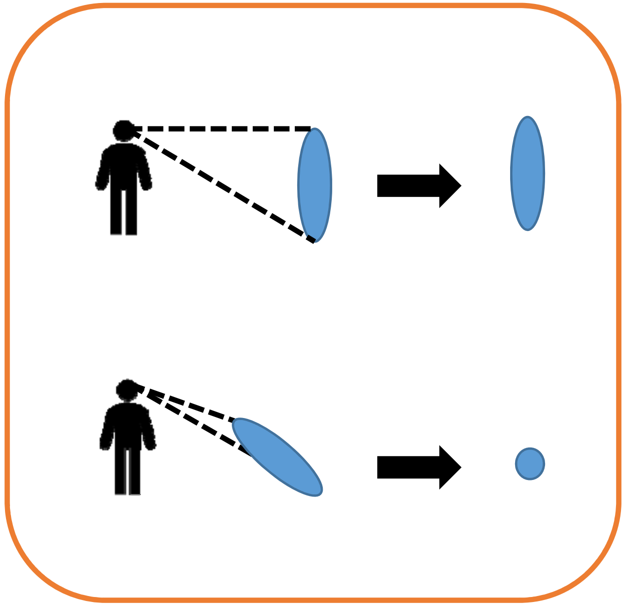
- Mechanism

1. 시료의 표면 물성치가 변화
2. 높은 반발 쇼크웨이브가 생성
3. 충격파 증가
4. 온도가 증가

LTE(Local Thermal Equilibrium)
$n_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3$ n_e : 전자 밀도 T : 온도
$N_e = C(N_e, T_e)\, \Delta\lambda_{FWHM}^{3/2}$
N_e : 전자 밀도 T_e : 온도 $\Delta\lambda_{FWHM}^{3/2}$: 반치폭

Measurement of gas flow rates by LIBS





- 레이저 유도 플라즈마의 형태는 주변 유체의 거동에 영향을 받음.
- 기체 유동에 의해 플라즈마의 관측방향이 변하게 되며, 형상계수 변화는 복사열전달에 관계되어 LIBS의 수집신호에 함수로 확인될 수 있음,