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Application of Response Surface Methodology to laser-induced breakdown spectroscopy: Influences of hardware configuration ☆

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Abstract

Response Surface Methodology (RSM) was employed to optimize LIBS analysis of single crystal silicon at atmospheric pressure and under vacuum conditions (pressure ~ 10^{-6} mbar). Multivariate analysis software (StatGraphics 5.1) was used to design and analyze several multi-level, full factorial RSM experiments. A Quality Factor (QF) was conceived as the response parameter for the experiments, representing the quality of the LIBS spectrum captured for a given hardware configuration. The QF enabled the hardware configuration to be adjusted so that a best compromise between resolution, signal intensity and signal noise could be achieved. The effect on the QF of simultaneously adjusting spectrometer gain, gate delay, gate width, lens position and spectrometer slit width was investigated, and the conditions yielding the best QF determined.

Keywords: LIBS; Response Surface Methodology; Silicon; Optimization; Hardware

1. Introduction

1.1. Initial comparison of LIBS under vacuum and atmospheric pressure

For a LIBS spectrum to yield useful information it must have sufficiently high resolution such that overlapping peaks may be resolved, and low background noise ensuring good sensitivity. Many hardware parameters affect the properties of the spectra obtained: laser wavelength, power, frequency and fluence, spectrometer input slit width, ICCD gate delay and integration time, gain, focal position relative to sample, ambient atmosphere and pressure etc. Initial comparison between LIBS spectra of single crystal silicon captured at atmospheric pressure and at a pressure ~ 10^{-6} mbar indicates a remarkable difference in both resolution and intensity, as shown in Fig. 1. If LIBS is conducted under vacuum conditions then the resolving power is greatly improved [1] due to lack of pressure broadening effects. The peak intensity [2] and the background continuum radiation are seen to diminish due to plasma expansion. Hardware optimized to produce usable spectra at atmospheric pressure no longer produces optimal spectra at lower pressures; although resolution has improved, the peak intensity has diminished.

The usual method of optimizing any experimental set-up is to adjust one parameter at a time, keeping all others constant, until the optimum working conditions are found. Adjusting one parameter at a time is necessarily time consuming, and may not reveal all interactions between the parameters. In order to fully describe the response and interactions of any complex system a multivariate parametric study must be conducted.

1.2. Response Surface Methodology

Response Surface Methodology (RSM) is a powerful statistical analysis technique which is well suited to modeling

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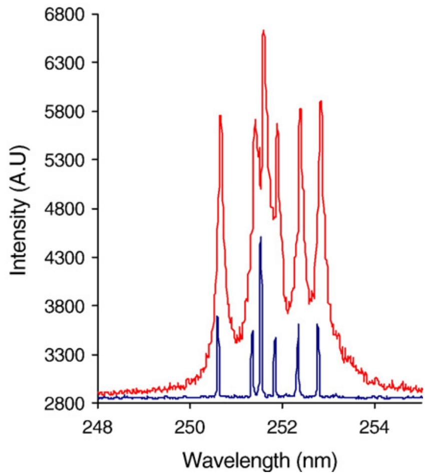

Fig. 1. Comparison of LIBS spectra obtained from laser ablation of silicon at atmospheric pressure (top trace) and under vacuum conditions (bottom trace).

complex multivariate processes, in applications where a response is influenced by several variables and the objective is to optimize this response. Box and Wilson first introduced the theory of RSM in 1951 [3], and RSM today is the most commonly used method of process optimization [4]. Using RSM one may model and predict the effect of individual experimental parameters on a defined response output, as well as locating any interactions between the experimental parameters which otherwise may have been overlooked. RSM has been employed extensively in the field of engineering and manufacture [5–11] where many parameters are involved in a process. RSM is now used widely in such diverse fields as microbiology [12,13], pharmacology [14], vehicle crash-testing [15], food chemistry [16], etc. RSM has been applied to the optimization of laser welding [17–20] and laser-cutting processes [21], but never before to optimization of LIBS hardware configuration.

In order to conduct any RSM analysis one must first design the experiment, identify the experimental parameters to adjust, and define the process response to be optimized. Once the experiment has been conducted and the recorded data tabulated, RSM analysis software models the data and attempts to fit a linear or second-order polynomial to this data.

1.3. Optimization of the RSM experiment

An un-optimized, multi-level full factorial experiment design requires all possible combinations of the experimental parameters to be considered. Increasing the number of parameters and also the number of levels (the variance of each parameter) will increase the number of analyses required as:

$$(\text{no. of levels factor } 1) \times (\text{no. of levels factor } 2) \times \ldots (\text{no. of levels factor } n) \quad (1)$$

The software package used in this study was StatGraphics 5.1, which is a highly specified multivariate statistical analysis package. StatGraphics 5.1 provides the capability to optimize a designed experiment. Optimization of an experimental design reduces the number of experimental runs required to model the response of a system, whilst retaining a comparable level of model accuracy. Algorithmic logic is used to estimate the minimum number of candidate runs required for the optimized design to adequately describe the system under investigation. The data obtained from the candidate runs is analyzed in the same manner as in a full experimental design. The fewer candidate runs one conducts, the less accurately the optimized design models the response of the full design. D-optimality is a criterion calculated by the design package and gives a measure of the variability of all the estimated parameters.

2. Experimental set-up

2.1. The LIBS apparatus

The apparatus shown in Fig. 2, was designed to be fully flexible and allow the LIBS analysis of solids, liquids and gases through a range of pressure regimes, from atmosphere down to $<10^{-6}$ mbar. The set-up includes a Nd:YAG laser (Continuum, Surelite), frequency doubled to produce an output at 532 nm, with 4–6 ns pulse length and a peak power of 200 mJ. The laser may be operated at repetition rates of up to 10 Hz, but for this investigation was limited to 1 Hz in order to reduce the gas load on the vacuum pump set. Laser radiation is focused onto the sample using a 300 mm convex lens that is mounted on a micrometer stage allowing positional adjustment along the axis of the laser beam of 30 mm either side of the focal position.

The sample is mounted in the vacuum chamber on an *x*–*y* stage so that each LIBS analysis can be performed away from previous ablation sites. The laser is focused onto the material under test inside the vacuum chamber through a quartz window mounted in a Con-Flat carrier. A Leybold TurboVac 50 turbomolecular pump backed by a Leybold TriVac rotary pump is used to evacuate the chamber to pressures $<10^{-6}$ mbar. A molecular sieve foreline trap was employed in order to reduce pump oil contamination back-streaming into the chamber.

Optical emission from the plasma plume is collected through a two metre fibre-optic cable, manufactured by Roper Scientific, with a wavelength range of 190 to 1100 nm. The fibre-optic cable is inserted into the vacuum chamber using a specially designed, elastomer sealed feed-through and is coupled to an Acton Research Spectra Pro 500i 0.5 m imaging triple grating (150, 600, 2400 lines mm^{-1}) spectrometer. The output of the spectrometer is coupled to an ICCD camera (PI-MAX, Princeton Instruments) that utilizes a proximity focused MCP intensifier connected via a fibre-optic coupling to the CCD array. The 1024×256 pixel CCD array is thermoelectrically cooled. A 1 ns increment in the gate delay and width is possible with a resolution of 40 ps. The laser power supply, camera and PC are connected to a programmable timing generator (Princeton Instruments ST-133A) denoted PTG on Fig. 2, enabling temporal resolution of the plasma plume. Roper Scientific's WinSpec/32 spectrum capture and manipulation software allows both capture of optical emission and identification of any prominent peaks present.