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Atomic emission stratigraphy by laser-induced plasma spectroscopy: Quantitative depth profiling of metal thin film systems

Tristan O. Nagy, Ulrich Pacher, Hannes Pöhl, Wolfgang Kautek*

University of Vienna, Department of Physical Chemistry, A-1090 Vienna, Austria

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ABSTRACT

Laser-induced plasma spectroscopy (LIPS) with a frequency-quadrupled Nd:YAG laser (266 nm, pulse duration: 4 ns) was applied to a metallic layer system consisting of an electrodeposited copper layer (30 μm) on an aluminium substrate. A stratigraphic model describing the emission signal in dependence of the pulse number was developed, which can explain several effects originating from laser ablation of various thin top layers by means of the Gaussian beam cross section character. This model was applied to trace elements through layers with thicknesses that are in the range of the resolvable depth, given by the single-pulse ablation rate, by means of empirical fitting functions. Additionally, the contribution of redeposited bulk material to the characteristic shape of emission-traces when averaging spot arrays with varying spacing could be quantified. This can be used to estimate cross-contamination in analytical applications where ablations need to be performed at close spacing.

1. Introduction

Laser-induced plasma spectroscopy (LIPS) has proven to be a valuable tool in industrial, biological, surface- and layer analysis [1,2]. *Stratigraphic* LIPS-investigations on multi-layer thin film systems, performed with nanosecond lasers in the infrared, visible and ultraviolet wavelength regime, offer a minimal invasive non-vacuum method for the determination of the thickness [3,4] chemical composition [5–7] and opto-physical behaviour [3] of films and coatings, for industrial [8,9], scientific [10,11] and conservation [12,13] applications.

The widely spread use of compact and low-cost high-power solid-state ns-lasers in stratigraphy requires investigations of the influence of the beam profile and experimental conditions on the ablation, incubation and plasma–emission behaviour. Laser–material interaction has long been discussed by different approaches [14–20]. Compositional depth profiling was treated empirically in respect to the irradiance dependence [3,21] and was modelled in detail [22].

Both the empirical and the theoretical approach have been successfully applied to the calculation and interpretation of depth profiles of layers which are relatively thick in comparison to the laser-ablation rate. However, for *thinner* layers the proposed models either yield no good fit to experimental data (in the case of the method proposed in [21]) or require substantial manual intervention in the fitting process [22], which is not desirable for a model intended for simple, widespread everyday application. The aim of this study was to find a practical mathematical model to describe signal behaviour of thin layers, providing usable results with reduced data processing effort.

Several ablation experiments were performed to characterise the laser–matter interaction of both constituent metals in a two-layer sample (copper on aluminium-substrate) by means of their ablation behaviour and the Gaussian beam shape. Then, several multi-spot stratigraphic measurements were used to calculate correlation depth profiles. In the third part, empirical fitting functions based on the Gaussian energy distribution of the laser beam as well as laser–plasma interaction were used to trace the metal signals through the layers, determine the emission profile and layer boundary and quantify the effect of cross contamination as a function spot distance and pulse energy.

2. Experimental

Model samples were prepared by polishing electron microscope sample mounts (Zeiss, ultra-pure Al, 1/2″⌀) to a roughness of 4000 mesh. These were electroplated in a 0.1 M copper sulphate solution (pH 7) with a current of 10 A dm^{-2} resulting in a deposition rate of 2.5 μm/12 min and thicknesses of 30 ± 3 μm and 50 ± 3 μm (used for threshold determination), respectively.

* Corresponding author. Tel.: +43 1 4277 52470; fax: +43 1 4277 52449.
E-mail address: wolfgang.kautek@univie.ac.at (W. Kautek).

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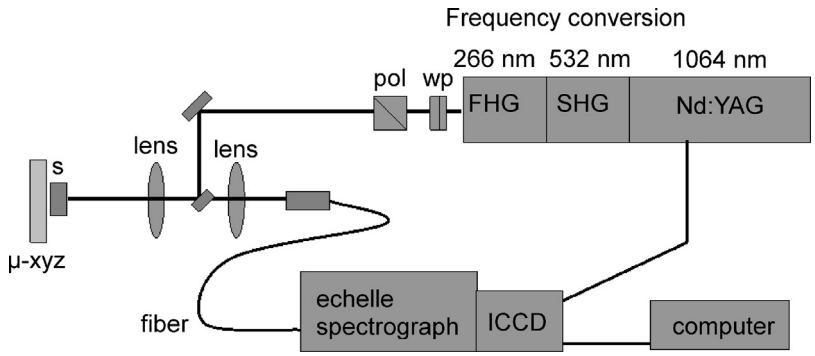

Fig. 1. Collinear ns-laser-induced plasma spectroscopy (LIPS) setup for 266 nm irradiation. s: sample. Pol: polariser. wp: 1/2-waveplate.

A frequency-quadrupled *Q*-switched Nd:YAG Laser (Quantel, model Brilliant EaZy) with $\lambda = 266$ nm and $\tau = 4$ ns was used. A plano–convex lens ($f = 92$ mm @ 266 nm) served for focussing the laser beam onto the sample. The depth of focus was calculated to be 0.159 mm. Samples could be moved with μm-stages in *x*, *y* and *z* (=beam-) direction.

A collinear LIPS-setup (Fig. 1) was developed for the opto-stratigraphic investigations. The same lens was used for laser focusing and light collection, allowing consistent imaging of the generated plasma plume for all ablation-depths [10,23]. The short laser wavelength made it necessary to couple in the laser via a small (1/2″⌀) mirror, instead of a wavelength selective beam splitter commonly used for IR and VIS lasers [23], because every suitable dichroic component would shade a major part of the spectrum. The plasma analysis was performed with an Echelle spectrograph (LTB Lasertechnik Berlin GmbH, model Aryelle 200) with an intensified and gated multichannel plate CCD camera (Andor, model ICCD 734 Gen II). For all measurements, the gate delay was set to 50 ns relative to the Q-switch trigger, and the gate width to 1 μs. For every depth profile 25 stratigraphic spot-measurements with 40 pulses per spot were recorded in order to improve the signal-to-noise ratio. Depth profiles were recorded at four different maximum pulse-fluences (120, 180, 230, and 290 J cm^{-2}) and four different spot spacings, 250, 500, 750 and 1000 μm, respectively.

The measurement of spot-diameters and-shapes as well as qualitative evaluation of the debris was done via optical (Olympus, model STM-MJS) and scanning electron microscopy (Zeiss, model Supra 55 VP). Diameters were evaluated by focusing the microscope on the (unmodified) surface and measuring the maximum distance between the inner borders of the melt mound along two perpendicular axes.

Elemental emissions were traced by calculating the linear correlation coefficient r ($-1 < r < 1$) of the averaged (25 single pulses) emission spectra with previously prepared standard spectra of the respective elements rather than measuring individual peak intensities. This method, commonly used in multidimensional spectroscopy uses *total spectral information* rather than single peak intensities by comparing all data points of an individual spectrum at a certain number of pulses *N* (and therefore a certain depth) to standard emission spectra acquired from pure elements. Fig. 2 shows one of the standards recorded by accumulating 100 single-pulse spectra on-chip before readout, with the most prominent emission lines labelled [24].

Since *r* can be assumed to be linearly proportional to the signal intensity as long as the signal-to-noise ratio (*S*/*N*) of the standard sample is substantially greater (≥2:1) than that of the experiment, this method is also a faster alternative to peak integration, which often turns out difficult at low intensities [21]. In addition, it provides good qualitative selectivity even for alloys or more complex substrates, where peak identification can be an issue.

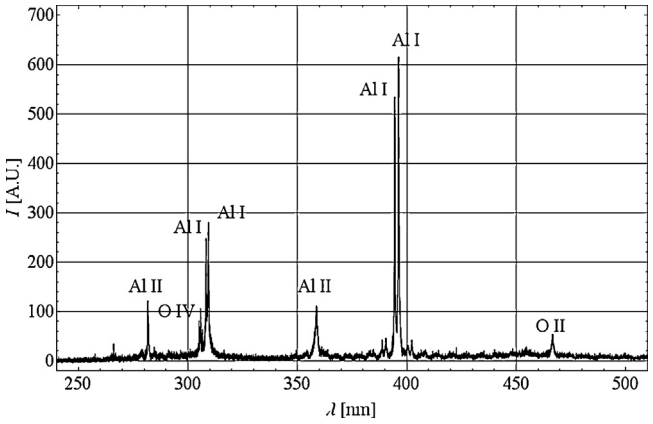

Fig. 2. Selected part of the Al standard spectrum used for correlation measurements, recorded at 120 J cm^{-2}. The most prominent emission lines are labelled, with roman numerals giving the degree of ionisation [24].

3. Results and discussion

3.1. Threshold determination and ablation behaviour

Ablation experiments with fluences from 20 to 500 J cm^{-2} yielded ablation–craters with diameters $D = 20$–90 μm at the bulk material, which are plotted against the applied laser peak-fluence

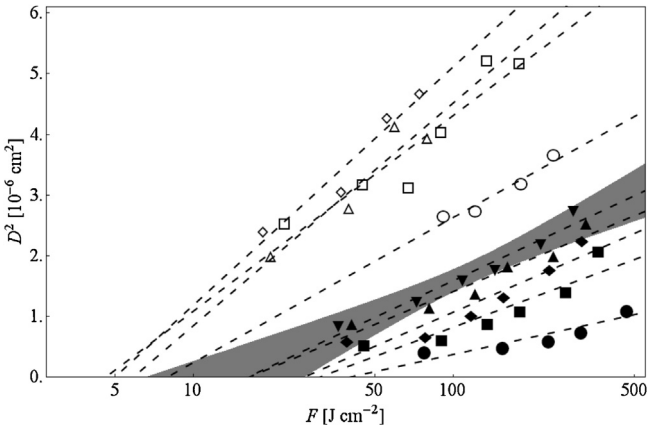

Fig. 3. D^2 vs. ln(F) plot of aluminium bulk-material. Different symbols represent different pulse numbers, ranging from $N = 1$ (●), $N = 2$ (■), $N = 3$ (♦), $N = 5$ (▲), $N = 10$ (▼), $N = 15$ (○), $N = 20$ (□), $N = 30$ (△), $N = 40$ (◊). The intercept on the ln(F) axis represents $F_{th}(N)$ according to Eq. (1). The grey area represents the 95% confidence interval for $N = 10$.