Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 83 (2016) 1329 – 1338

Physics Procedia

9th International Conference on Photonic Technologies - LANE 2016

Inline plasma analysis as tool for process monitoring in laser micro machining for multi-layer materials

Rouwen Kunze[a,]*, Guilherme Mallmann[a], Robert Schmitt[a,b]

[a]*Fraunhofer Institute for Production Technology IPT, Steinbachstr. 17, Aachen, Germany*
[b]*Laboratory for Machine Tools and Production Engineering WZL, RWTH Aachen University, Aachen, Germany*

Abstract

Laser micro machining is an innovative manufacturing technology with a wide range of processable materials and a high level of flexibility. Especially for processing multi-layer materials it is a tool for surface structuring and subsequent functionalization. The manufacturing of e.g. conductor paths for solar cells or batteries requires specific ablation depths on multi-layer materials in order to reveal conducting layers as functional conductor paths. To achieve an ablation of a specific, layer an in-line process monitoring can be used to warrant a robust manufacturing preventing damage on further surface layers. With regards on the need of material specific ablation parameters, this paper addresses the development of a measurement system based on laser induced breakdown spectroscopy (LIBS) as a tool for real-time process monitoring by in-line plasma analysis. The presented results show the specific plasma emission variation at layer interfaces, which can be used for real-time feedback process control with the goal of minimizing the ablation of further layers.

Peer-review under responsibility of the Bayerisches Laserzentrum GmbH

Keywords: Laser induced breakdown spectroscopy; plasma analysis; laser emission spectroscopy; in-line metrology; real-time feedback

1. Introduction and motivation

Laser micro machining processes are present today in a large number of industrial applications and are mainly set-up by process know-how for their process stability and reproducibility. Nevertheless, considering the usage of short and ultra-short pulsed lasers, laser micro machining systems present a high degree of material independence

* Corresponding author. Tel.: +49-241-8904-573 ; fax: +49-241-8904-6573 .
E-mail address: rouwen.kunze@ipt.fraunhofer.de

Peer-review under responsibility of the Bayerisches Laserzentrum GmbH
doi:10.1016/j.phpro.2016.08.140

associated to the ability to remove small amounts of matter from the workpiece's surface [Chichkov et al. 1996]. These characteristics lead to applications addressing e.g. the structuring and functionalization of surfaces [Zhao et al. 2014, Booth et al. 2006] as well as in the processing of single or multi layered as well as thin layered surfaces [Dligatch et al. 2004]. Multi-layered surfaces as an accumulation of different materials layered in one workpiece are very suitable to be manufactured by lasers because the material independence of laser manufacturing processes. In addition the structuring of thin layered structures under consideration of varying depth and width profiles benefits from the potential of laser micro machining to ablate only small amounts of material from the workpieces' surface.

Just as laser micro machining, multilayers are spread in several industrial sectors. Some of the main applications are in products in the photovoltaic, display, LED, OLED and battery areas [Mank and Mason 1999, Morita et al. 1988, Yeh 1986, Hermann et al. 2006]. In most of the process chains connected to these products the production of the multi-layer components requires a finishing or patterning step as last process step. In most cases this last step is used for defining form and edges of the produced multi-layered component or to interconnect or isolate its different layers.

Especially in the manufacturing of high performance surface structures for layered materials the usage of patterning techniques based on laser micro machining delivers both technical and financial advantages. However inherent aspects of the laser ablation associated to workpiece variations resultant from previous processes can lead to overall process instabilities. Furthermore, different machine, workpiece and environmental related parameters can also influence the process stability and reproducibility. In special, possible result variations due to thickness variations on different layers and material dependent laser removal lead to an unknown penetration depth and consequently to a possible damaging to underlying layers or even to an incomplete removal of a specific layer. All these possible process deviations can cause adverse functional impacts or even lead to rejects.

To secure process stability and quality for long periods the usage of a process monitoring associated to a feedback control is indispensable. Therefore this paper examines the possibilities of a laser process related plasma emission analysis for a process dependent layer material detection and discrimination.

2. Concept

2.1. Measurement principle

The laser induced breakdown spectroscopy (LIBS) focuses on the spectroscopic evaluation of plasma arising by the laser ablation of materials [Cairns and Kaiser 2014]. This principle of LIBS can be applied in a wide range of applications and materials. Possible applications of LIBS are the material characterization of uniform materials and compositional mapping of heterogeneous materials. An antecedent application for compositional mapping from which LIBS was originated is the determination of the originality of works of art without damaging the high valuable objects. Another application is depth profiling, which determines the material composition in axial direction of the laser optics, while compositional mapping examines the material composition in lateral direction [Gottfried and De Lucia, 2010]. As laser source for the plasma generation, short pulsed and ultra-short pulsed laser sources are used. Laser micro machining processes based on these laser sources generate also plasma, which can be used similarly to the normal LIBS applications.

The physical phenomena occurring during this procedure will be described below, with main focus on the plasma breakdown and its spectral characterization.

The plasma breakdown as basic physical process for the measurement signal origination is a laser related and process dependent phenomenon which is fixed permanently to laser ablation processes. The laser induced plasma is therefore also a by-product of laser machining processes containing the ablated material and the remaining energy delivered by the laser. Basically the plasma breakdown expires over several steps strongly influenced by the laser pulse irradiation. For short pulsed laser sources, the procedure starts with the impact of the laser pulse on the materials' surface, where the material in the laser spot gets firstly heated. Followed by the vaporization of an amount of material, regarding the laser parameters, a plume of ablated material arises which is further heated by remaining laser irradiation with a subsequent ionization of the ablated atoms and molecules induced due to different ionization processes correlating with the induced laser pulse energy. After forming the ionized plasma plume, containing the ablated material as stimulated ions, processes of recombination occur in the laser induced plasma which leads finally

to the decay of the plasma plume. This plasma decay and recombination indicates the actual measurement signal by discharging the induced energy by the recombination of the certain ions back to their normal atomic or molecular structures. The released energy due to the recombination of the ions is an electric magnetic wave in the spectrum of light. Both the plasma evolving and decay process are illustrated in Fig. 1.

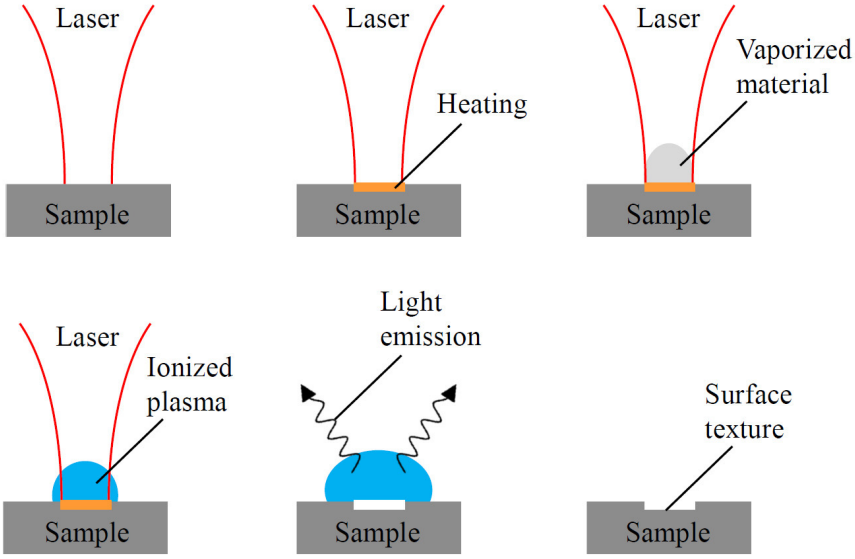

Fig. 1. Schematic illustration of the plasma expansion mechanism, induced by laser irradiation and subsequent followed by the vaporization and ionization of the ablated material and the recombination of the plasma with the characteristic light emission [Adapted from Bohling et al. 2010].

The specific ionization properties [Noack and Vogel 1999] and their following recombination, allocate a specific energy discharge to certain materials by the rearrangement of the excited electrons back to their atomic cites [Capitelli et al. 2004]. Therefore for each particular material, a certain recombination energy occurs, delivering consequently light with a different spectral characteristic for unequal materials [Aden et al. 1993, Anisimov et al. 1974].

Resort on these characteristic properties of laser induced plasma as a by-product for laser ablation processes the spectroscopy of the plasma emission can lead to an identification of the actually processed material. This is realized by the optical diffraction of the emitted plasma spectrum into its containing wavelength dependent shares. By the evaluation of the spectra, certain materials can be identified by their specific plasma emission curves.

2.2. Inline plasma monitoring

Based on the principle properties outlined in the previous section the positive characteristics of the LIBS technology generates an extended capability for monitoring laser processes and feeding actual information back to the laser manufacturing process. This ability enables inline process parameter supervision for laser processes in a large field of applications. The usage of an unused by-product as source for the measurement signal within LIBS enables a simple set-up and system integration of into laser micro machining units without requiring a separate form of signal generation as e.g. an additional light source.

In this context the main measurement modules of a LIBS system are a light collecting unit to couple emitted plasma light into the measurement system and a spectrometer as evaluation unit for the collected spectra.

Regarding the radiation properties of the emitted light related to the plasma, a light collecting unit based on focusing parabolic off-axis mirrors is used for coupling the plasma emission into a fibre guiding the light into the spectrometer. The schematic set-up of the light collecting unit is demonstrated in Fig. 2.

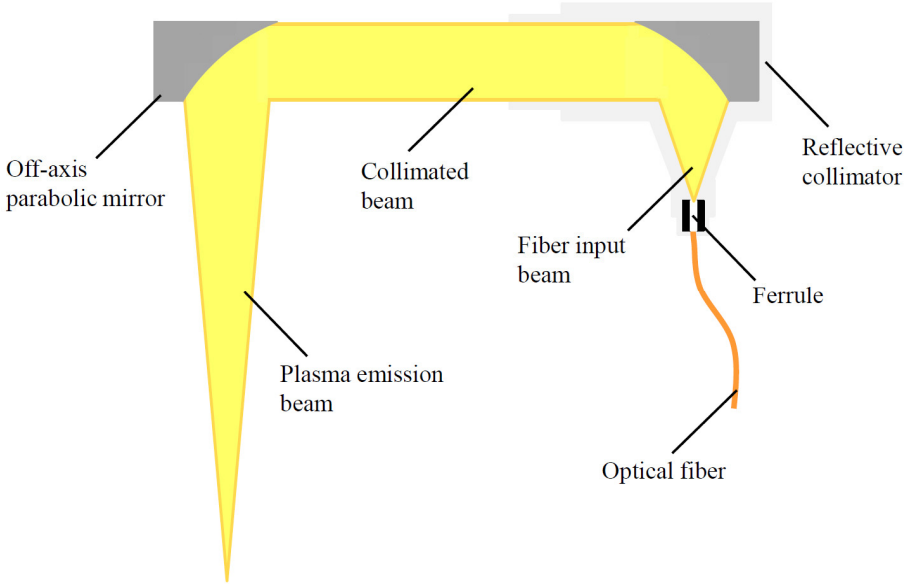

Fig. 2. Schematic composition of the light collecting unit, composed of an off-axis parabolic mirror, a reflective collimator and an optical fibre.

The fibre coupled plasma emission gets carried into the spectrometer where it is passed over to an open beam and impinges onto a holographic concave diffraction grating, which executes the spectral diffraction. The concave grating moreover focuses the diffracted light onto a CCD camera line to translate the lights' intensity distribution over the wavelength into the plasma emission curve. The measured intensities distributed over the spectrum are unique to certain materials and indicates the actual ablated material composition. Fig. 3 shows the schematic set-up of the spectrometer used of the LIBS system.

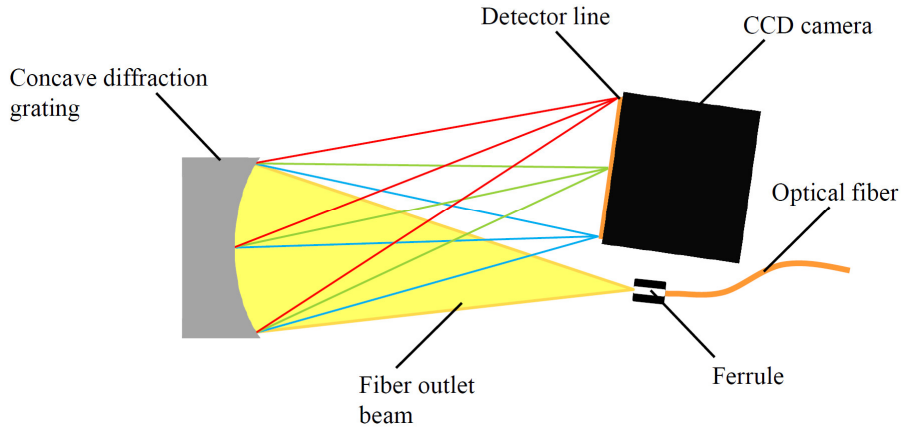

Fig. 3. Schematic composition of the spectrometer, composed of the fibre outlet aperture, a concave holographic grating for the spectral decomposition and a CCD line camera for light detection.

3. Experimental set-up

3.1. Measurement system prototype

The measurement system set-up was designed based on an adapted light collecting unit and an optimized spectrometer. Therefore the light collecting unit was implemented with two parabolic off-axis mirrors one for collimating the plasma emission to the second mirror which focuses the light again on the aperture of an optical fibre. The fibre used for guiding the LIBS plasma emission signal to the spectrometer was a multi-mode fibre on the purpose of transmitting the plasma emission light with low spectral dependent absorption. Another reason is to achieve high intensities on the spectrometers' line detector. Therefore a core diameter of 200 µm was chosen. The spectrometer connected to the light collecting unit due to the optical fibre, was set-up with the fibre aperture as light entrance to bring the collected light in a divergent beam onto the functional diffraction surface of the grating. The concave holographic diffraction grating requires a divergent beam in a predefined incidence distance and angle to focus the light in a focal plane in a certain emergence distance and angle. In addition the functionally graded surface structure of the grating diffracts the light into its spectral intensity distribution and moreover corrects optical aberrations like the field of curvature, coma and astigmatism. The grating delivers the light with an angle of emergence of 12.1° and a distance of the focal plane of 107.6 mm, resulting from a line density of 600 lines per mm. The concave holographic grating furthermore was chosen because of its bright wavelength correction. Starting in the spectral range of UV, covering the whole VIS spectrum and at last has a little contingent of the NIR. The described grating is with a corrected spectral range of 190 nm to 750 nm very suitable for applications in LIBS, as most materials have their plasma emission in the UV and VIS spectrum. A selection of materials and their plasma emission lines are shown in Table 1 [Ismail et al. 2004, Tong et al. 2004, Sturm et al. 2004, Bassiotis et al. 2001, Russo et al. 2012]. As a detector a silicon based line camera was used with responsivity from 300 nm to about 950 nm. All components therefore were chosen with regards to a wide spectral functionality and sensitivity to develop a system capable of measuring many different materials with differing plasma emission lines.

Table 1. Laser induced plasma emission lines of relevant elements for laser machining.

Element	Main emission lines		
Iron (Fe)	375,8 nm	271,5 nm	187,8 nm
Nickel (Ni)	225,4 nm		
Chromium (Cr)	286,3 nm		
Molybdenum (Mo)	281,6 nm		
Aluminum (Al)	394,4 nm		
Copper (Cu)	521,8 nm	324,8 nm	
Carbon (C)	193,1 nm		

3.2. Laser micro machining system with integrated plasma monitoring

The plasma monitoring experiments were realized by test measurements during laser structuring processes with the integrated laser induced breakdown spectrometer into a laser micro machining system. The applied laser was a nanosecond fibre laser with a centre emission wavelength of 1064 nm, pulse durations between 4 ns and 200 ns and pulse repetition frequencies between 1.6 kHz and 1000 kHz. The average output power of the laser system is about 1 mJ per pulse. The laser is focused on the manufactured sample surface by a telecentric f-Theta objective with a working distance of 79.4 mm. The deflection of the laser is carried out via a laser scanner with a position velocity of 15 m/s, a repeat accuracy of less than 2 µrad and an aperture of 10 mm. The measurement system was integrated with the assembled light collecting unit off-axis to the laser beam. The off-axis integration was done by allocating the focal point of the light collecting parabolic off-axis mirror right into the ablation area of the laser. The focus of the mirror allocated in the laser scan field results in the feature of collecting the plasma emission light, originating in the focal point of the mirror. An amount of the light which arises in the scan field due to the laser pulse impacts and

the following ablation process radiates in the direction of the mirror and gets coupled into the light collecting unit. The measurement system and its integration are shown in Fig. 4.

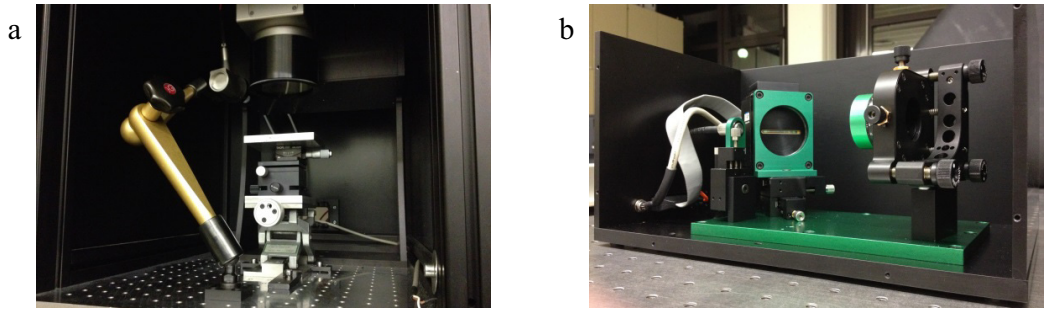

Fig. 4. (a) Integration of the measurement system via the light collecting unit; (b) Optical set-up of the spectrometer.

3.3. Experimental definitions

For the evaluation of the LIBS measurement system firstly experiments with two different materials were performed to characterize in the first place the spectral width and sensitivity of the measurement system via a bright steel spectrum. Steel plasma emits a bright spectrum because of its composition of several alloying elements. The used steel sample of 45NiCrMo16 will therefore emit the emission lines of iron, chromium, molybdenum and nickel outline in Table 1. In a second step the resolution of the system will be evaluated with aluminum plasma which is supposed to emit a strong and single emission line at 394.4 nm because it contains from only one element. Then the capabilities of the LIBS measurement system to make a qualitative discrimination between different materials of multi-layered surfaces were evaluated by structuring a carbon coated copper foil with the following measurement and spectral characterization of the induced plasma plumes for the different layers.

The used laser process parameters were chosen regarding the materials' ablation properties. For manufacturing steel and aluminum the laser micro machining systems is adjusted on pulse duration of 200 ns, repetition frequency of the pulses of 45 kHz and scanning steps of 10 µm, which leads to a pulse energy of 0.35 mJ. The low repetition rate has to be adjusted in this magnitude depending on a long pulse duration, which in turn leads to a higher amount of energy per pulse. The small scanning steps are supposed to generate a tightly packed area for the pulses to impact. This should lead to a larger quantity of emitting plasma plumes in the focal point of the light collecting unit. The laser parameters are chosen in this configuration to achieve preferably high emission intensities of the emerging plasma plumes. Regarding the collection of the plasma emissions, the settings of the camera are adjusted for a good detection of the spectral emission values by the camera as well. The camera exposure time is set to 55.25 µs and is configured to that value to achieve a sufficient illumination time on the detector line regarding the laser pulse energy. The exposure time of 55.25 µs represents the highest possible exposure time of the camera in the combination with its maximum frame rate of 18000 Hz. With these parameters a high frame rate frequency is enabled, which leads to the acquisition of a high number of spectral images over the single iteration steps during the ablation of every present material layer. For both the laser process parameters and the camera preferences the same configuration is used for measuring steel as well as aluminum. For the manufacturing of the carbon coated copper foil and the subsequent plasma examination both the laser and the camera parameters had to be adapted to the changed process requirements. The laser parameters are adjusted only in terms of pulse energy, which was set to 0.04 mJ. Therefore the pulse duration of 200 ns as well as the repetition frequency of 45 kHz and the scanning steps of 10 µm were left unchanged. The changes are well suited for both the ablation of carbon and copper. Regarding the reduced pulse energy the camera parameters have to be adapted as well. Due to the lower plasma emission intensities resulting from the lower pulse energy, the camera parameters are set to the maximum value for the exposure time of about 3124.7 µs, which results in a maximum possible value of the frame rate of 320 Hz.

4. Results

Fig. 5 presents the resulting intensity distribution of the measured LIBS over the spectrum of light for the selected steel alloy sample.

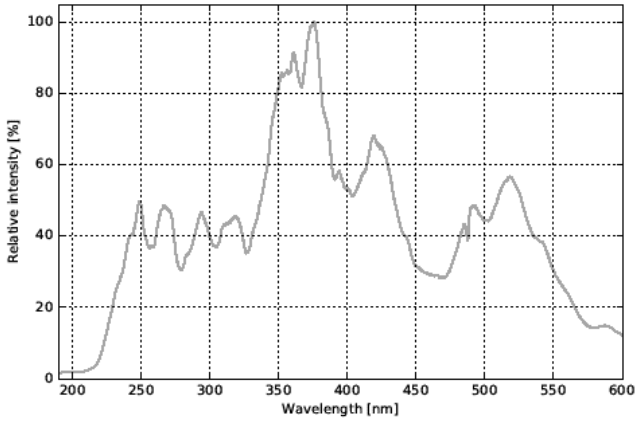

Fig. 5. Intensity for LIBS plasma emission spectrum for the selected steel alloy sample.

The LIBS spectrum of the steel sample shows the typical bright spectrum, located in the VIS and UV spectrum of light regarding to a qualitative comparison to reference spectra, which were published by other authors [Ismail et al. 2004, Tong et al. 2004, Sturm et al. 2004, Bassiotis et al. 2001, Russo et al. 2012] and summarized in Table 1. In accordance with the references, the spectrum of steel displays its strong emission peak for Iron in the UV region around the expected wavelength of 375.8 nm, which is qualitatively demonstrated by the measured spectrum. Chromium with its peaks at 286.3 nm and 267.7 nm and Molybdenum with its main emission peak at 281.6 nm are qualitatively visualized in the spectral range between 250 nm and 350 nm [Sturm et al. 2004]. Only the expected peaks of Carbon and Nickel are not enclosed in the measured spectrum. Their emission peaks were expected to appear at 193.1 nm for Carbon and 225.4 nm for Nickel. The absence of the Carbon and Nickel peak, which are supposed to be in the spectral region beneath 250 nm indicates the limit of the developed LIBS systems' spectral sensitivity. Restricted by the responsivity of the camera the spectral sensitivity of the LIBS system reaches from about 250 nm to 600 nm which is shown in the steel spectrum in Fig. 5. This validation can be made because the spectrum clearly acquired the emission peaks of Iron, Chromium and Molybdenum in their expected spectral range.
After the characterization of the spectral sensitivity of the developed LIBS system, experiments to characterize the spectrometers' resolution were carried out. This characterization was made by measuring the plasma emission spectrum of aluminium which is expected to emit a strong and thin emission line located at 394.4 nm [Sturm et al. 2004]. The measured spectrum shows clearly the expected aluminium plasma emission. Except the expectation of a very thin emission line [Sturm et al. 2004] the LIBS system integrated in the laser micro machine shows the peaks qualitatively in the correct spectral range but blurred over a spectral range of 20 nm around the original peak at 394.4 nm for the main peak of aluminium. This blurring effect limits the spectrometers' resolution, which means that peaks must be separated at least 20 nm from each other to be discriminated by the LIBS system. Furthermore some other minor peaks are detected which are induced mainly due to the oxide layer of aluminium which emits peaks at 310 nm and 520 nm [Ismail et al., 2004]. These peaks can clearly be separated from the main aluminium peak which is shown in Fig. 6. The other occurring peaks in both the steel and aluminium spectrum are most likely the result of impurities of the materials.

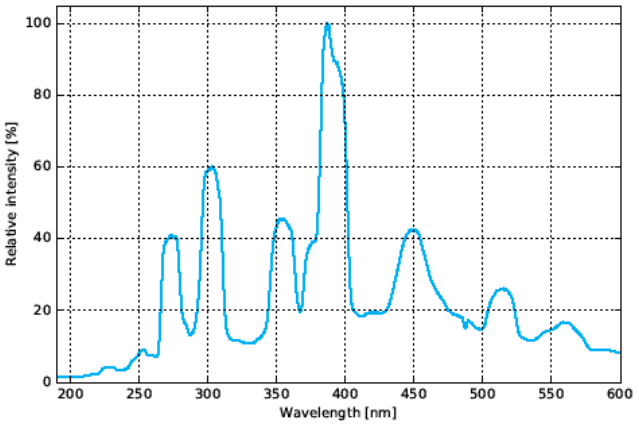

Fig. 6. Intensity for LIBS plasma emission spectrum of the selected aluminum sample.

Besides the previous experiments on the spectral sensitivity and resolution of the LIBS system, a statement over its capability of discrimination between different surface layer materials was made. The two measured graphs in Fig. 5 and Fig. 6 deliver a clearly qualitative discrimination between the two materials. For further validation of the systems' capability to distinguish between different layers of multi-layered surfaces a third sample was examined during a laser micro machining process. The measured plasma emission spectra of the carbon coated copper foil are illustrated in Fig. 7 and Fig. 8.

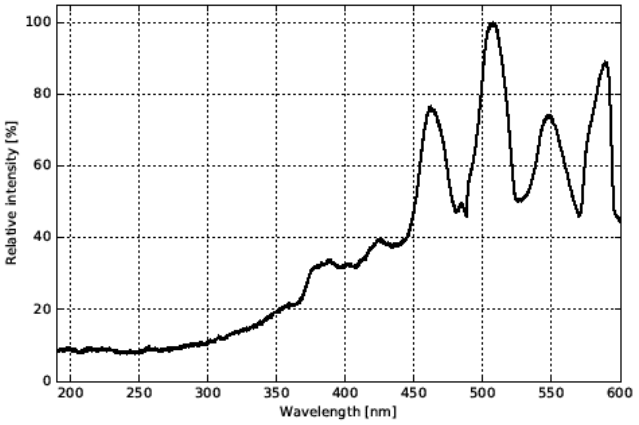

Fig. 7. LIBS intensity spectrum for carbon before ablating through the transition zone of the carbon coated copper foil.

The low energy pulses, described in section 3.3, enables an ablation over three pure Carbon ablation iterations, until the Carbon layer is fully ablated and Copper arises in the spectrum. The plot of the last carbon spectrum, before the transition zone gets ablated, and the first copper spectrum, after the transition zone has been removed, show a significant qualitative differentiation between the two spectra. This leads to the conclusion, that the LIBS system can detect the transition zone between two thin layered materials in terms of an ablation with several laser pulse iterations and therefore the removing of a thin single layer each per pulse. Besides the good capability of the system to distinguish between the two layers the emission line of carbon at 193.1 nm is not detectable as is was in the steel spectrum. The spectral sensitivity limited by the camera can be declared as the reason for the missing carbon.

However, the spectrometer detects some peaks in the VIS spectrum from about 450 nm to 600 nm, wherefore only the presence of Carbon in a different condition regarding its atomic lattice gives an explanation. The detected emission lines most likely occur from C_2 as Riascos et al. 2004 pointed out. By the recombination of C_2 the plasma is expected to irradiate its emission between 400 nm to 600 nm [Riascos et al. 2004], which is qualitatively congruent with the spectrum in Fig. 7. After the exceeding the ablation plane over the interface between the two material layers, the spectrum shown in Fig. 8 occurs. The pictured spectrum contains the same characteristic emission peaks like the literature points out for Copper. The spectrum contains one peak in the lower UV, which fits the described emission line of 324,8 nm [Sturm et al. 2004] and another peak in the VIS spectrum at 521,8 nm, which is congruent with the publications of another author [Tong et al. 2004]. For this reason the LIBS system can be declared of being capable of the detection and characterization of Copper as well.

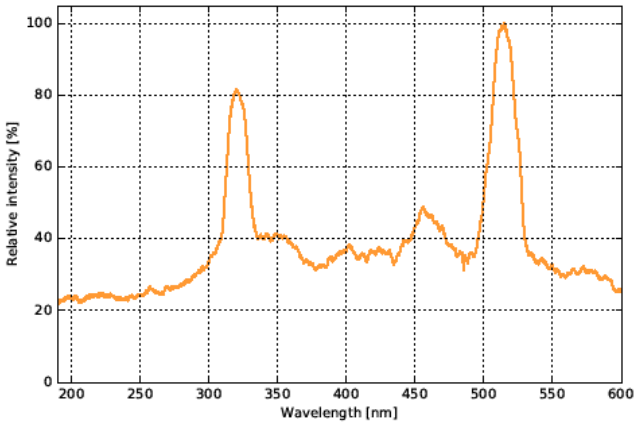

Fig. 8. LIBS intensity spectrum for copper after ablating through the transition zone of the carbon coated copper foil.

For matching the different declarations of the references, the conclusion can be made, that the measured spectrum of a Carbon coated Copper substrate by a LIBS system fits the characteristic emission lines of the composing materials and is furthermore capable of differentiate different materials due to an ablation process of a series of laser pulse iterations.

5. Conclusion and outlook

Nowadays real-time feedback control systems for laser micro machining applications are still not state of the art. Laser micro machining is mainly set-up by empirical methods for its process stability and depends in wide areas on control systems, which jeopardizes the ablation processes in terms of a proper defined surface modelling and traceability. Considering the previously described workpiece, machine and environmental related overall variations, which affect the process robustness and the final product quality, a process monitoring and control is however demanding in several areas. In the special case of the machining of layered surfaces with laser ablation, the feedback of the ablation depth as well as layer change would enable an increase of the overall process robustness. For this reason the possibilities of laser induced breakdown spectroscopy as a feedback control system for laser micro machining applications for multi-layered surfaces were evaluated.

The technology of LIBS provides in contrast to other measurement systems the fundamental capability of the material and consequently layer change detection also for thin layers, because LIBS uses the plasma, which is induced by the laser machining process itself and is in addition independent of restrictions due to its optical components in a wide range. LIBS uses the mechanisms of laser induced plasma, which provides the possibility of measuring the material composition of the ablated material, collecting real-time information about the laser process. The provided information is feedback right to the laser micro machining system enabling the adaption of its

parameters optimizing the current ablation situation. The developed system demonstrated its capabilities of measuring different samples with a subsequent identification of the containing materials by the examination of the plasma emission spectra. Even though the measurement system reached its limitations regarding spectral sensitivity and resolution, all system parameters are suitable for the detection and discrimination of plasma emission spectra of a wide range of materials relevant for laser micro machining applications. Furthermore the flexibility of the LIBS set-up of being adaptable to specific boundary conditions enables this technology for a wide range of applications.

There is however still room for improvement besides the spectral sensitivity and resolution. This applies especially for the aspect of feedback control. Therefore the focus on the further development of the LIBS unit for laser process monitoring is the creation of a signal processing software which can provide a feasible regulating of the laser process, protecting the underlying layers of multi-layered surfaces from being ablated by the appearance of the first differing spectrum from the actual processed materials' spectral distribution.

References

Chichkov, B. N., Momma, C., Nolte, S., von Alvensleben, F., and Tünnermann, A., 1996. Femtosecond, picosecond and nanosecond laser ablation of solids. Applied Physics A, 63(2):109-115.

Booth, H., 2006. Techniques and Applications of Laser Micro-Processing at the Micron and Sub-Micron Level. Conf. on Lasers and Electro-Optics.

Zhao, X., Cao, Y., Nian, Q., Cheng, G., Shin, Y. C., 2014. Control of Ablation Depth and Surface Structure in P3 Scribing of Thin-Film Solar Cells by a Picosecond Laser. J. Micro Nano-Manufacturing 2(3).

Dligatch, S., Netterfield, R. P., 2004. Real time process control and monitoring in multi-layer filter deposition. Optical Interference Coatings, OSA Technical Digest Series.

Mank, A. J. G. and Mason, P. R. D., 1999. A critical assessment of laser ablation ICP-MS as an analytical tool for depth analysis in silica-based glass samples. Journal of analytical atomic spectrometry, 14(8):1143-1153.

Morita, N., Ishida, S., Fujimori, Y., and Ishikawa, K., 1988. Pulsed laser processing of ceramics in water. Applied Physics Letters, 52(23):1965-1966.

Yeh, J. T. C., 1986. Laser ablation of polymers. Journal of Vacuum Science & Technology A, 4(3):653-658.

Hermann, J., Benfarah, M., Bruneau, S., Axente, E., Coustillier, G., Itina, T., Guillemoles, J.-F., and Alloncle, P., 2006. Comparative investigation of solar cell thin film processing using nanosecond and femtosecond lasers. Journal of Physics D: Applied Physics, 39(3):453.

Cairns, G. and Kaiser, J. (2014). Automated 2D elemental mapping by laser-induced breakdown spectroscopy.

Gottfried, J. L. and De Lucia, Jr, F. C. (July 2010). Laser-induced breakdown spectroscopy: Capabilities and applications.

Bohling, D. C., John, A., and Cordts, L., 2010. Sensoren auf Basis der Laserinduzierten Breakdown-Spektroskopie (LIBS) für industrielle Anwendungen.

Noack, J. and Vogel, A., 1999. Laser-induced plasma formation in water at nanosecond to femtosecond time scales: calculation of thresholds, absorption coefficients, and energy density. IEEE Journal of Quantum Electronics, 35(8):1156-1167.

Capitelli, M., Casavola, A., Colonna, G., and De Giacomo, A., 2004. Laser-induced plasma expansion: theoretical and experimental aspects. Spectrochimica Acta Part B: Atomic Spectroscopy, 59(3):271-289.

Aden, M., Kreutz, E. W., and Voss, A., 1993. Laser-induced plasma formation during pulsed laser deposition. Journal of Physics D: Applied Physics, 26(10):1545.

Anisimov, S. I., Kapeliovich, B. L., and Perelman, T. L., 1974. Electron emission from metal surfaces exposed to ultrashort laser pulses. Zh. Eksp. Teor. Fiz, 66(2):375-377.

Ismail, M. A., Imam, H., Elhassan, A., Youniss, W. T., and Harith, M. A., 2004. LIBS limit of detection and plasma parameters of some elements in two different metallic matrices. Journal of analytical atomic spectrometry, 19(4):489-494.

Tong, T., Li, J., and Longtin, J. P. (2004). Real-time control of ultrafast laser micromachining by laser-induced breakdown spectroscopy. Applied Optics, 43(9):1971-1980.

Sturm, V., Vrenegor, J., Noll, R., and Hemmerlin, M., 2004. Bulk analysis of steel samples with surface scale layers by enhanced laser ablation and LIBS analysis of C, P, S, Al, Cr, Cu, Mn and Mo. Journal of analytical atomic spectrometry, 19(4):451-456.

Bassiotis, I., Diamantopoulou, A., Giannoudakos, A., Roubani-Kalantzopoulou, F., and Kompitsas, M., 2001. Effects of experimental parameters in quantitative analysis of steel alloy by laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 56(6):671-683.

Russo, R. E., Bol'shakov, A. A., Yoo, J. H., and Gonzalez, J. J., 2012. Laser ablation plasmas for diagnostics of structured electronic and optical materials during or after laser processing. Proc. SPIE, pages 82430A-82430A-7.

Riascos, H., Zambrano, G., and Prieto, P., 2004. Plasma characterization of pulsed-laser ablation process used for fullerene-like CNX thin film deposition. Brazilian Journal of Physics, 34(4B):1583-1586.