Analysis of minor elements in steel and chemical imaging of micro-patterned polymer by laser ablation-spark discharge-optical emission spectroscopy and laser-induced breakdown spectroscopy

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ABSTRACT

Laser ablation - spark discharge - optical emission spectroscopy (LA-SD-OES) and Laser-induced breakdown spectroscopy (LIBS) are applied for the analysis of minor elements Manganese (Mn) and Chromium (Cr) in steel and for the chemical imaging of micro-patterned photoresist layers. In LA-SD-OES a weak laser pulse (typical energy 50 μJ to 5 mJ) triggers an electric discharge between a high voltage electrode and the laser ablated spot on the sample surface. Intense emission lines of neutral and singly-ionized atoms are observed with both spectroscopic techniques. However, lines of doubly-ionized atoms are detected with LA-SD-OES only. The line intensities of C III and Al III increase with decreasing laser pulse energy, surprisingly. The appearance of intense doubly-ionized lines indicates that the mechanisms of plasma excitation are different in LA-SD-OES compared to LIBS and that the combined plasma is not in local thermodynamic equilibrium at low laser energy. The calibration curves of Mn and Cr in industrial steel reveal steeper slope (higher sensitivity) for the Mn II and Cr II lines measured with LA-SD-OES and for the Mn I and Cr I lines measured with LIBS. Chemical imaging of the photoresist layer with LA-SD-OES at the atomic lines of C I and C III and the molecular band of CN reveals all details of the sample. Similar images are obtained for C I and CN using LIBS, however, no image contrast is obtained at the C III line. The very low pulse energy in LA-SD-OES enables soft sampling and may be beneficial also for the analysis and imaging of sensitive material.

1. Introduction

The detection of chemical elements and the quantification of material compositions are important in many areas of materials research, chemistry, and physics and for many different applications, for example, in industrial production and for materials inspection and sorting. Different analytical techniques aiming for fast and reliable element quantification are available and new techniques are being developed. Optical emission spectroscopy (OES) offers minimal invasive multielement detection which can be applied even in harsh environmental conditions. In spark-OES, a plasma is induced by an electric spark discharge to the surface of the sample material and the optical plasma emission is measured [1]. This technique has become one of the standard methods, especially for element analysis of metallurgical materials [2,3]. Commercial manufacturers are providing dedicated equipment for spark excitation and for optical detection [4,5]. In laser-induced breakdown spectroscopy (LIBS) the analytical plasma is excited by pulsed-laser ablation of sample material and the optical emission of the laser-induced plasma (LIP) is measured [6–8]. LIBS is employed for in-line measurements of various materials in industrial production, e.g. of steel [7], mineral melts [9], steel slag [10,11], coal [12,13], rubber [14], refractory materials [15], waste electric and electronic equipment WEEE [15], scrap metal [7,16], and waste plastic [17,18]. Other field applications include the on-site analysis of geological materials at the Earth’s surface [19] at the sea floor in deep sea [20], and on Mars [21]. Recent progress in the analytical and industrial applications and the fundamentals of LIBS can be found in the literature [6–8,22]. Comparative studies on LIBS and spark-OES showed comparable analytical...
2.1. Experimental setup

In order to enhance the optical emission from the LIP several re-excitation sources such as double and multiple laser pulses [25,26] and microwave [27–29] or radiofrequency radiation [30] are under investigation. The combination of laser ablation and electric discharge for plasma excitation and emission enhancement was demonstrated also [31]. This method re-gained attention in recent years and high voltage spark discharges have been reported to enhance the optical line emission [32–34], to increase the signal-to-background ratio (SBR) and the signal-to-noise ratio (SNR) [31,35], and to improve the sensitivity [36] and the limit of detection (LOD) [37,38]. Also, an enhanced emission of molecular lines was observed in spark assisted laser ablation molecular isotopic spectrometry (LAMIS) [39]. Laser ablation - spark discharge - optical emission spectroscopy (LA-SD-OES) uses the method of combined plasma excitation. In LA-SD-OES the spark discharge is strongly localized to the position of the laser spot on the sample surface. The localization of material sampling and analysis enables chemical imaging of inhomogeneous samples with high spatial resolution [40]. For the re-excitation of LIP by a pulsed electric discharge different geometrical arrangements of electrodes and sample have been investigated. Spark discharge between two electrodes close to the laser-ablated spot enables to analyze electrically insulating materials. The two electrodes can be arranged in a line and placed parallel to the sample surface [31,39]. Alternatively, one electrode may be positioned at oblique angle to the surface [41] or both electrodes may be placed at an angle to the sample resulting in a “V” shaped arrangement [42]. The “V” shaped and the parallel arrangement of electrodes have been compared [42]. A larger amount of ablated material for a “V” shaped discharge channel and a strong increase of line intensities with applied voltage for a discharge channel parallel to the sample have been observed. For the analysis of electrically conductive materials one electrode may be applied and the spark is directed to the sample which is kept at ground potential, typically. The electrode can be positioned perpendicular to the sample surface if the laser beam is under oblique angle of incidence. In comparison to other techniques for intensity enhancement like microwave and cavity assisted LIBS, the spark-assisted LIBS technique is rather simple and versatile and it enables to detect higher ionized species. Double-pulse (DP) LIBS and spark-assisted LIBS have some features in common like better stability and higher SNR of emission line intensities as compared to conventional single-pulse LIBS [34,35]. For the determination of carbon in soil a higher sensitivity of spark-assisted LIBS compared to DP-LIBS was observed [43].

In this paper, we report on LA-SD-OES and LIBS measurements of steel and aluminum bulk samples. This study is a starting point to evaluate the analytical performance of LA-SD-OES and to compare it with LIBS and spark-OES. We measure LA-SD-OES and LIBS spectra and observe a qualitatively different dependence of emission line intensities on the laser pulse energy. Calibration curves of minor elements in steel are obtained with both techniques. The LA-SD-OES spectra reveal spectral lines not observed with LIBS. This enables for LA-SD-OES chemical imaging of polymer thin film samples using emission lines that do not provide image contrast in LIBS.

2. Experimental

2.1. Experimental setup

Fig. 1 presents a schematic of the setup. The optical emission is induced either by laser ablation (LIBS) or by the combination of laser ablation with electric spark discharge (LA-SD-OES). For the experiments a Nd:YAG laser at the fundamental wavelength λL = 1064 nm (Litron, pulse duration τL = 6 ns, pulse energy EL ≤ 100 mJ, repetition rate frep ≤ 100 Hz) was employed. A beam expansion system (1:1 to 3:1) comprised of two lenses was used. The energy of laser pulses was measured with a “FieldMax II-P” energy meter (Coherent). For energies below 1 mJ the laser beam was attenuated using neutral density filters. The transmission of filters was measured with a spectrophotometer. The laser pulses were focused perpendicularly onto the sample to ablate target material and to induce a plasma. A biconvex glass lens of focal lengths f = 50 mm was used for focusing of the laser radiation. The diameter of the laser focal spot was in the range of 100 μm if not stated otherwise. For the electric discharge a pointed tungsten (W) electrode rod (Plansee SE, 99.97%, diameter 2 mm, tip radius of curvature 0.18 mm) was placed close to the laser focal spot on the sample surface. The horizontal distance between electrode tip and laser beam was kept as small as possible, limited by shadowing of the laser beam. While the horizontal distance between electrode and laser spot was only about few 100 μm, the vertical distance was typically in the range of 1 to 2 mm. High voltage of up to 3 kV from a laboratory power supply (Ortec) was applied to the electrode via a load capacitor with capacitance of C = 25 nF and a load resistor with resistance of R = 1 MΩ. The sample acted as cathode to avoid ion bombardment and ablation of the electrode [44]. The resulting electric field was below the electrical breakdown field strength (typ., Ebr ≈ 3 kV/mm in ambient air [45]). The laser-induced plasma (LIP) produced seed electrons and triggered the ignition of the electric spark. The high voltage applied to the electrode tip rapidly decayed in the spark discharge and it revealed few strongly damped oscillations until complete discharge approx. 1 μs after the spark ignition. Positioning of the samples on a 2D xy-translation stage provided the possibility for lateral scanning procedures and chemical imaging experiments. The translation stage was equipped with computer-controlled stepper motors. Further experimental details are reported elsewhere [40]. The sample surface was in the focal plane of the focusing lens (vertical direction z). A 30 mm focusing lens collected the plasma radiation and coupled it into a quartz glass fiber. The collecting lens was aligned to the laser spot on the sample surface and light emitted from the plasma volume covered by the collection optics was detected (spatial filtering was not employed). The quartz glass fiber was connected to a compact Czerny-Turner type spectrometer with a spectral range from about 200 to 460 nm and a spectral resolution of approx. 0.145 nm (Avantes AvaBench 2048, variable delay time td, integration time 2 ms).

2.2. Sample materials

Two types of sample materials were investigated. The first type was industrial steel samples provided by the steel producing company voestalpine Stahl GmbH (Austria). Eleven steel samples with different
concentrations of minor and trace elements were measured to establish calibration curves with LIBS and LA-SD-OES. Reference analyses of the element compositions were performed with spark-OES by voestalpine Stahl GmbH. For the minor elements manganese and chromium the concentration range was from 0.19 to 2.1 wt\% and from 0.018 to 2.4 wt\%, respectively. The Fe concentration was above 95 wt\% for all steel samples. The second type of sample materials were polished aluminum metal slabs covered with an approx. 1.3 μm thin spin-coated photoresist (PR) layer. The aluminum slab was polished with sandpaper and diamond suspension. Before covering with PR, the slab was rinsed in acetone and acetic acid. For the imaging experiments only parts of an aluminum slab were covered with the PR. The PR layer was micro-patterned by UV photo-lithography using a standard mask (USAF-1951 resolution test chart, MIL-STD-150A) and developer (MF319).

2.3. Sample preparation and measurement procedure

The steel samples were mechanically milled and cleaned with acetone before the experiments. Several tens of single measurements were performed, each on a different position at the sample surface. The spectra were collected with an integration time of 2 ms and a delay time of \( t_d = 0 \text{ ns} \) (Fig. 4a) and 300 ns (Fig. 4b). With LA-SD-OES the spectral line intensities of singly-ionized Fe spectral lines have higher intensity with LA-SD-OES than with LIBS, than 1200 Fe I-II lines in the range 290–315 nm \([46]\). Singly-ionized Fe spectral lines (Fe I at 247.86 nm) was visible in spectra with both techniques, the doubly-ionized carbon (C III) line at 229.69 nm was detected with high intensity only with the additional spark ignition and at low laser pulse energy. Singly-ionized carbon (C II) spectral line intensities appeared much higher with the spark discharge. The measurements were conducted at different laser pulse energies with a spectrometer delay of \( t_d = 0 \text{ ns} \) (Fig. 4a) and 300 ns (Fig. 4b). With LA-SD-OES the spectral background was very low at both delay times and the observed spectral lines had higher intensity at \( t_d = 0 \text{ ns} \). The high signal/background ratio raises the possibility of ungated spectrochemical investigations which are not possible with LIBS. The LIBS spectra at 0 ns delay exhibited high spectral background and high shot-to-shot intensity fluctuations, especially at high laser pulse energy. In averaged LIBS spectra a weak C III peak raised above the high background. The influence of the laser pulse energy on the spectral line intensities is described in Section 3.2.

Spectra of industrial steel samples were measured with both techniques at a fixed laser pulse energy of 5 mJ (Figs. 5 and 6). The spectra reveal a complex structure due to the high number of Fe lines (more than 1200 Fe I-II lines in the range 290–315 nm \([46]\)). Singly-ionized Fe II spectral lines have higher intensity with LA-SD-OES than with LIBS, similar to the observations on the aluminum and aluminum/photoresist samples.
samples. The neutral Fe I spectral lines exhibit equal intensities with both techniques. In order to visualize the positions of Fe I and Fe II lines in measured spectra, the calculated LIBS spectra received from [46] for electron temperature $T_e = 1$ eV and electron number density $N_e = 1 \times 10^{17}$ cm$^{-3}$ are shown for comparison (NIST in Figs. 5 and 6). Two Fe II lines are clearly separated from Fe I lines and the intensity of Fe II lines is higher with LA-SD-OES (Fig. 6). Besides Fe, the minor elements Mn and Cr were detected. The concentration in this steel sample was $C(\text{Mn}) = 0.786$ wt% and $C(\text{Cr}) = 0.991$ wt%.

3.2. Dependence of line intensities on laser pulse energy

The influence of laser pulse energy on the spectral line intensities in LA-SD-OES and LIBS was determined. A photoresist coated Al slab was measured at different laser pulse energies. Figs. 7 and 8 show the intensities of C and Al lines as a function of the laser pulse energy, respectively. The mean of the background-subtracted intensities was established out of 160 single measurements per laser pulse energy. The standard deviations are represented by error bars. Due to the very low spectral background in LA-SD-OES the spectra were recorded at delays of 0 ns (Figs. 7a, 8a) and 300 ns (Figs. 7b, 8b). LIBS measurements were performed with 300 ns delay due to the high background and large fluctuations at zero delay (Figs. 7c, 8c). For LA-SD-OES the laser pulse energy was low and ranged from 12 μJ to 85 mJ. The plasma was very weak and no lines were observed in LIBS spectra at 1 mJ energy.

The intensity of the C III line (229.69 nm) of the PR layer showed an unexpected exponential increase with decreasing laser pulse energy in LA-SD-OES (Fig. 7a, b). The shot-to-shot variation of intensity was relatively large. At 1 μJ the C III line vanished. The C I line intensity (247.86 nm) stayed nearly constant over the presented energy range and it increased at higher levels (up to maximum laser energy). The fluctuation of the C I line intensity was relatively small. The singly-ionized carbon lines (C II, 251.21 and 283.67 nm) showed intensities that initially increased and then
decreased with increasing energy (not shown). In LIBS, the C I line intensity increased monotonously with laser energy and the doubly-ionized C III line was very faint. Also the doubly-ionized Al III lines (360.19 and 361.24 nm) of the metal substrate revealed exponentially increasing intensities for decreasing laser energy when measured with LA-SD-OES (Fig. 8 a, b). The Al I and Al II line intensities were minimum at around 0.25 mJ and they increased strongly (moderately) at lower (higher) pulse energy. The different energy dependence of the C I-II and Al I-II lines in LA-SD-OES was probably due to strongly different ablation rates for the bulk aluminum substrate and the thin PR layer. In the LIBS spectra the Al I and II lines were present at any pulse energy but Al III lines were not detected.

The C III and C I line intensities measured with LA-SD-OES at 12 μJ pulse energy are shown in Fig. 9. Each data point corresponds to the intensities measured in one spectrum and in total approx. 90 spectra were evaluated. At zero delay (td = 0 ns) the C III and C I intensities were high in most of the spectra and the data points were strongly clustered (Fig. 9a). The bar charts in red and black colour show the histograms of C I and C III intensities, respectively. The histograms revealed a Gaussian-like distribution of signals. For delayed detection (td = 300 ns) the C III lines showed larger shot-to-shot intensity fluctuation and a correspondingly broader distribution in the histogram (Fig. 9b). Very similar results were obtained also at 20 μJ pulse energy. In LA-SD-OES a lag time tlag between laser pulse and spark discharge was observed that depends on laser pulse energy, on electrode-sample distance, and on the applied electrode voltage [40]. At zero delay time the fluctuations of the lag time do not influence the measured spectra (2 ms integration time). For delayed detection fluctuations of tlag may have caused the broadened distributions of measured line intensities.

3.3. Calibration curves of minor elements in steel

The minor elements chromium (Cr) and manganese (Mn) in eleven industrial steel samples were measured by LA-SD-OES and LIBS and the calibration curves obtained with both spectrochemical techniques were compared (Mn: 0.19 to 2.1 wt%; Cr: 0.018 to 2.4 wt%). The laser pulse energy was 1 mJ and 5 mJ for LA-SD-OES and 5 mJ and 80 mJ for LIBS. 120 measurements per sample and per laser pulse energy were conducted. Several spectral lines from neutral and singly-ionized atoms of Cr and Mn were evaluated. Fig. 10 shows the normalized spectral line intensity as a function of the element concentration measured with both techniques at 5 mJ laser energy. The spectral line intensity above the background was divided by the mean intensity of the overall spectrum. The error bars indicate the standard deviation of spectra, each spectrum being averaged over 10 measurements. Fig. 10a and b represent calibration curves for the Mn II line at 293.93 nm and the Mn I line intensity at 354.78 nm, respectively. The calibrations for Cr II at 312.04 nm and Cr I at 359.35 nm are presented in Fig. 10c and d, respectively. The calibration curves for Mn II and Cr II are linear and show a higher slope with LA-SD-OES in comparison to LIBS. For the neutral atomic lines, LIBS resulted in calibration curves with steeper slopes. For the resonant Cr I line at 359.35 nm the calibration curves are non-linear (Fig. 10d). The deviation from linearity is most likely due to radiation self-absorption in the plasma. This conclusion was supported by a calculation of the plasma absorption parameter \( \kappa_t \) for the Cr I and Cr II lines [11]. The absorption is two orders of magnitude larger for the resonant Cr I line, i.e. \( \kappa_t(\text{Cr I}) = 1.46 \times 10^{-28} \text{ m}^3 \) and \( \kappa_t(\text{Cr II}) = 2.01 \times 10^{-30} \text{ m}^3 \) at plasma temperature \( T_e = 7000 \text{ K} \). The calibration curves measured with LA-SD-OES at 1 mJ and with LIBS at...
80 mJ laser pulse energy exhibit lower slopes and lower correlation coefficients of the fits as compared to the measurements with 5 mJ.

Table 2 summarizes the results of the LA-SD-OES and LIBS calibration for Mn and Cr in steel for several neutral and singly-ionized emission lines and different laser energy. Linear regression lines were fitted to background-subtracted peak intensities and the obtained slopes of regression lines were tabulated. The highest slope (sensitivity) was obtained at 5 mJ laser energy for both techniques (numbers printed in bold). The asterisk symbol indicates non-linear calibration curves. The LOD was estimated with LOD = 3 σ/k where σ is the standard deviation of the peak intensity of the analyte with the lowest concentration and k the slope of the calibration curve. For Cr the lowest LOD of 0.065 wt% is obtained with the Cr II line at 312.04 nm measured by LA-SD-OES with 5 mJ. With LIBS the LOD of Cr is 0.235 wt%.

3.4. Chemical imaging using neutral and higher ionized emission lines

Chemical imaging of a sample surface by LA-SD-OES and LIBS is enabled by the strongly localized plasma excitation in both techniques. In LA-SD-OES, the spark discharge is triggered by laser ablation and directionally guided to the LIP [40]. For imaging a polished aluminum sample with a photoresist pattern of the USAF-1951 chart on the surface was raster-scanned with LA-SD-OES and LIBS. The scanned surface was approx. 20 x 14 mm and more than 27,000 single spectra were collected with a repetition rate of 3 to 4 Hz. A very low laser pulse energy of 60 μJ was applied for the LA-SD-OES measurements. In LIBS the laser pulse energy was 9.6 mJ. The step size of the raster scan was 100 μm. The gray scale heatmaps in Fig. 11 display three different spectral line intensities and their spatial variation across the sample surface. The background intensity was subtracted before evaluation to mitigate the
influence of shot-to-shot intensity fluctuations which were much higher with LIBS than with LA-SD-OES. For the neutral carbon line at 247.86 nm the LIBS and the LA-SD-OES spectrochemical images show clear features of the USAF PR pattern (Fig. 11a, b). High and low spectral line intensities were represented as dark and bright colored pixels, respectively. The image contrast is higher with LA-SD-OES than with LIBS. The doubly-ionized C III was detected only with LA-SD-OES and the image taken at 229.69 nm reveals all details of the PR pattern (Fig. 11c) while the LIBS image does not show any structure (Fig. 11d).

For the CN molecular emission with the UV band head at 388.3 nm the spectrochemical images reveals clear intensity contrast for both techniques, LIBS and LA-SD-OES (Fig. 11e, f).

LIBS measurements at a lower laser pulse energy of 4.6 mJ did not produce images with significant contrast for the three spectral lines investigated (C I, C III, CN). Optical microscopy images of the PR-coated aluminum samples after raster scanning exhibited a crater size of about 40 μm for LA-SD-OES and of about 100 μm for LIBS. Further imaging experiments with LA-SD-OES and a step size of 40 μm was performed. A PR stripe pattern with 100 μm lateral spacing was clearly resolved in the LA-SD-OES images.
The main difference between LA-SD-OES, LIBS, and spark-OES techniques is the process of excitation of analytical plasma. In LIBS, a laser pulse ablates material from the sample and induces the plasma. In spark-OES the plasma is excited by electric discharge applying a strong electric field (above breakdown field strength). The sampling and plasma formation is a single-step process in both techniques. In LA-SD-OES, a laser pulse triggers an electric spark discharge between the electrode and the sample which excites the plasma. The spark lags behind the laser pulse [40] and the formation of plasma can be considered as a two-step process. The laser pulse ablates sample material and the electric spark excites plasma of high luminosity.

The main advantages of LA-SD-OES compared to LIBS are the induction of analytical plasma at low laser pulse energy and the detection of doubly-ionized emission lines with high signal/background ratio. For a laser energy \( E_L = 10–100 \mu J \) and a spot area \( A = 0.01 \text{ mm}^2 \) the fluence \( F = 0.1–1 \text{ J/cm}^2 \) is well below the threshold fluence \( F_{th} \) for nanosecond laser ablation of metals (several J/cm², typically [49]). The weak laser pulse desorbs / ablates material from within the irradiated spot and a thin layer on the surface of the sample. This spatially confined sampling supports chemical imaging with high spatial resolution. Laser pulses of medium to high energy as applied in LIBS, typically, give craters of larger diameter and depth which may be less beneficial for high resolution imaging. The doubly-ionized species in LA-SD-OES are detected with high SBR at relatively long detection delays. In conventional single-pulse (SP) LIBS such lines are usually very weak and very rapidly decaying. In double-pulse (DP) LIBS, the SBR of such lines is usually higher than in SP LIBS but this emission is still very rapidly decaying and it can be detected only at very short detection delays where intensity fluctuations are large [50,51].

Typical experimental parameters employed in LIBS and LA-SD-OES are summarized in Table 3. The volume of plasma was roughly estimated from the time-integrated optical photographs (Fig. 2) and used to determine the order of magnitude of the plasma energy density and power density. For a more accurate determination of the plasma size time-resolved spectral images of plasma could be measured. Both techniques enable localized spectrochemical analysis. Sampling of material is restricted to the laser ablated area in LIBS and in LA-SD-OES the spark is directionally guided to the focused laser spot on the sample surface (Fig. 2).

4.1. Emission from higher ionized species

For each sample material the emission spectra and the absolute line intensities measured with LA-SD-OES and LIBS were similar. However,
the relative line intensities of neutral and ionized atoms were different. In LA-SD-OES the singly-ionized lines had much higher intensities and the neutral lines had similar intensities in comparison with LIBS at the same laser pulse energy (Figs. 3 to 6). Optical emission from doubly-ionized atoms was detectable only with LA-SD-OES at low energy of the trigger laser pulse. The relative line intensities could not be explained by the emission of plasma in local thermodynamic equilibrium (LTE) [40]. The spark discharge enhanced the intensities of higher ionized lines most likely due to collisional electron impact ionization in the plasma [44]. At higher laser pulse energy the intensities of doubly-ionized lines decreased exponentially (Figs. 7, 8). The amount of laser-ablated material and the size of laser-induced plasma increased with laser energy while the lag time of laser-triggered spark discharge decreased. This affects the electron impact ionization of plasma species in the spark discharge and may support the thermalization of the analytical plasma. A decreasing signal enhancement for neutral and singly-ionized lines with increasing laser energy was observed earlier [34,42]. The re-heating of plasma by the electric discharge was considered to decrease with increasing laser energy [34]. On the other hand, the dependence of ablated mass on laser energy was considered to be responsible for the smaller enhancement at higher pulse energy [42].

The observed intensity enhancement of ionized lines could be connected to a possibly different amount of ablated mass and number of emitting species in LA-SD-OES compared to LIBS. The craters produced by one laser pulse in LIBS and one laser pulse and electric spark in LA-SD-OES were measured with optical microscopy and optical profilometry (white light interferometer). At moderate laser pulse energy $E_L = 5 \text{ mJ}$ the craters on bulk aluminum samples had same diameter (approx. 100 μm) and same depth for both techniques. At low pulse

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Fig. 11. Spectrochemical images of USAF test pattern in photoresist layer on aluminum substrate measured by LA-SD-OES (a, c, e) and by LIBS (b, d, f). Laser pulse energy was 60 μJ for LA-SD-OES and 9.6 mJ for LIBS. Images obtained from the neutral carbon C I line intensity at 247.9 nm (a, b), the doubly-ionized C III line intensity at 229.7 nm (c, d), and the CN violet band head intensity at 388.3 nm (e, f). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
energy $E_L = 20 \mu J$ the craters on bulk aluminum samples coated with
photosensit layer (1.3 \mu m thick) had a diameter of approx. 15 \mu m in
LIBS and approx. 30 \mu m in LA-SD-OES. From this we conclude that the
spark discharge (energy approx. 78 mJ) probably increases the amount
of ablated material at low laser energy. However, the same crater size
observed at moderate laser energy (5 mJ) indicates that the energy of the
spark discharge is predominantly coupled to the laser-induced plasma re-exciting the plasma species. Part of the spark energy is
probably dissipated in the sample. Typically, remelting of sample ma-
terial is observed in spark-OES [1].

Recent publications on spark enhanced LIBS experiments assumed plasma in LTE condition and calculated the electron temperature $T_e$
using the Boltzmann plot method [32,34,52]. Higher $T_e$ and electron number density $N_e$ with additional spark discharge [53] and a stronger increase of $T_e$ at lower laser energy were reported [33]. On the other hand, the same $T_e$ in LIBS plasma with and without spark was reported earlier [31]. Furthermore, deviations from LTE state in spark-LIBS plasma were reported in a very recent publication and $T_e$ determined from Al I and Al II lines as well as the electron and ion temperatures were different for measurements in vacuum [54]. The line intensity ratios measured in our experiments performed in ambient air indicate non-LTE plasma at low laser pulse energies.

### 4.2. Sensitivity

The calibration curves for minor elements Mn and Cr in steel exhibit higher slopes with LA-SD-OES than with LIBS when evaluating spectral lines of singly-ionized atoms (Fig. 10, Table 2). For the emission lines of neutral atoms the slopes are higher with LIBS. The ionization in the spark discharge increased the intensities of singly-ionized lines and was responsible for the steeper slope (higher sensitivity). The estimated limits of detection in these first experiments are of the same order of magnitude with LA-SD-OES and LIBS. In a recent publication the major elements Cr (2–29 wt%), Mo (5–28 wt%), and Fe (1–14 wt%) in stainless steel were analyzed by spark discharge assisted LIBS [32]. The calibration curves had higher slope when the additional spark discharge was applied to the laser-induced plasma which is in qualitative agree-
ment to our results. A lower slope of calibration curves in spark-assisted LIBS was observed for minor elements in aluminum alloys [55]. The normalized line intensities (minor element/major element) were eval-
uated and an excitation probability that is different for major and minor elements was concluded. An earlier study compared the sensitivity of LIBS and spark-OES for minor and trace elements in steel and similar results were reported for both techniques [24].

### 4.3. Chemical image contrast

Hyperspectral imaging can be performed both with LA-SD-OES and with LIBS by scanning the sample under investigation with respect to the laser beam spot. The 2D (lateral) and 3D (lateral and depth) imaging is possible. A higher image contrast of the photosensit sample was obtained in LA-SD-OES compared to LIBS measuring the C I line at 247.86 nm (Fig. 11 a, b). With conventional spark-OES the imaging is not feasible as the electric spark is impacting randomly on the sample surface and not on a selected point of analysis. With LA-SD-OES higher ionized spectral lines are detected and element images and chemical information can be obtained that may not be accessible with LIBS under typical measurement conditions (C III line at 229.69 nm, Fig. 11 c, d). Another advantage of LA-SD-OES is the very low laser pulse energy that is sufficient to trigger the spark discharge. At lower energy the crater size on the sample surface decreases and smaller step sizes for scanning can be applied in order to achieve higher spatial resolution. A line pattern in the photoresist sample with line separation of about 100 \mu m was clearly resolved by LA-SD-OES imaging at very low laser pulse energy (0.06 mJ) and reduced step width (40 \mu m).

### 5. Conclusion

The combination of pulsed-laser ablation and electric spark dis-
charge for the excitation of analytical plasma and optical emission spectroscopy is promising for element analysis and chemical imaging. Compared to conventional spark-OES the directional guidance of the laser-triggered spark enables chemical imaging with high spatial re-
solution by the LA-SD-OES technique. Compared to LIBS the much lower laser pulse energy (\mu J range) enables for soft sampling of material by LA-SD-OES. The detection of higher ionized lines in LA-SD-OES opens an additional spectral window for analysis that is usually not accessible in LIBS. Elements with spectrally overlapping emission lines of neutral and singly-ionized species could eventually be separated and the OES analysis of materials be improved. This study was also aiming to compare the analytical performance of LA-SD-OES and LIBS. For the investigated minor elements in steel we obtain higher sensitivity for the singly-ionized atoms using LA-SD-OES and higher sensitivity for the neutral atoms using LIBS. Our future developments will include the optimization of electronic circuitry of the spark generator (voltage, frequency, pulse shape) and the use of a spectrometer with higher spectral resolution in order to increase the LA-SD-OES signals and the SNR and to provide better spectral separation of major and minor/trace element lines. Measurements in different gas background are planned.

### Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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