

Optical characterization of a co-planar dielectric barrier discharge as plasma source for element detection in analytical chemistry

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Abstract: Within this work a discharge design in shape of a co-planar surface dielectric barrier discharge is characterized as a tool for trace element detection in analytical chemistry. Since helium metastables play an important role in the dissociation process of the analyte molecules, helium metastable densities were measured by tunable diode laser absorption spectroscopy. Basic discharge dynamics were characterized by spatially, temporally and spectrally resolved optical emission spectroscopy.

Keywords: dielectric barrier discharge, optical emission spectroscopy, tunable diode laser absorption spectroscopy, analytical chemistry

1. Introduction

In recent years, numerous designs of dielectric barrier discharges (DBD) were established in the field of analytical chemistry. Due to their versatility, they are used in many different applications. One example is the detection of elements at very low concentrations in the range of ppb or ppt in a liquid sample. However, this can be quite challenging, since for common DBD designs the introduction of a liquid into the discharge results in the extinction of the plasma. One way to extract analyte from a liquid sample using plasma is the flowing liquid atmospheric pressure glow discharge [1]. This configuration enables the ignition of the plasma directly on top of the liquid surface. A disadvantage of this technique is that the extraction of the analyte is only from the top layer of the liquid. For hydride forming elements, such as arsenic, selenium or tellurium a different approach can be applied. By means of the hydride generation technique (HG) the analyte from the liquid sample forms a gaseous hydride, which can be introduced into a plasma. HG is very efficient and reaches conversion rates close to 100 %. A well-studied discharge design in combination with HG is the planar DBD introduced by Kratzer et al [2]. The DBD comprises of a hollow T-shaped quartz glass body with two planar parallel electrodes sputtered on top of the glass. The discharge gas such as helium or argon in combination with the analyte hydride molecule is flushed through the inlet arm. By applying a square wave or sinusoidal voltage of up to 7 kV at 20 kHz to the electrodes, a plasma can be ignited. The discharge operates as an atomizer, which dissociates the hydride molecule. The free analyte atoms can subsequently be detected by different diagnostic methods such as atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS) or optical emission spectroscopy (OES). The common atomization technique is the heated quartz tube atomizer (QTA) [3] consisting of a quartz tube heated up to a temperature of around 900 °C, which causes dissociation of the analyte molecules. The great advantage of using the DBD instead of the QTA is, that this heating is not necessary, thus minimizing the

requirements on the setup regarding temperature robustness.

In previous studies, temporally and spatially resolved OES has been performed on the planar DBD operated in helium in combination with different analytes, which revealed the basic plasma dynamics and showed that helium metastables play an important role in the dissociation of the analyte molecules [4,5].

However, by means of AAS it was shown that for a few hydride forming elements, such as bismuthine and lead the DBD shows much worse detection limits than for other elements, such as arsenic or selenium. This is accompanied by pronounced deposits of the analyte on the inner wall of the DBD. Comparable deposits could also be observed with arsenic as analyte with low applied power. By increasing the power, the deposits were removed by the plasma. This indicates an intricate balance between analyte deposition and removal. Under ideal conditions, more analyte atoms are removed than deposited, resulting in a high analyte concentration in the plasma and a low detection limit for the species. Therefore, in this work, we present a co-planar DBD design, which forces the plasma in a bent structure close to the walls of the quartz body, facilitating an enhanced removal of the analyte from the wall. The discharge dynamics of the bent structure is studied by temporally and spatially resolved OES and is compared to the behaviour of the common parallel electrode design. Moreover, metastable densities are measured with tunable diode laser absorption spectroscopy to correlate the helium metastable density to the spatial emission signal of the plasma.

2. Experimental setup

DBD device and electrical setup. The DBD used in this work consists of a hollow T-shaped quartz glass body similar to the arrangements used in previous works for the planar design. However, instead of the planar electrodes on each side, two parallel line-shaped gold electrodes were deposited on one outer side of the quartz body. The discharge design is shown in the dotted square in Fig. 1.

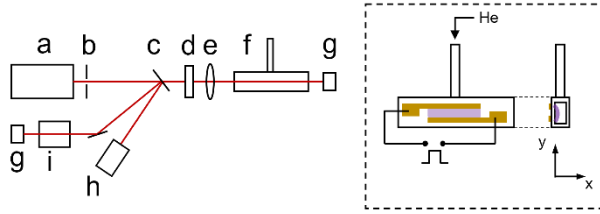


Fig. 1. Experimental arrangement of the TDLAS setup and a scheme of the discharge design in the dotted square

To ignite a plasma, a square wave voltage of around 2.75 kV is applied to the electrodes with a frequency of 20 kHz. The voltage is supplied by an in-house built generator. Two optical setups were used to study the discharge.

Tunable diode laser absorption spectroscopy (TDLAS). By means of TDLAS, the helium metastable density is estimated. A brief sketch of the setup is shown in Fig. 1. The laser light originates from a tunable diode laser head (a), which is tuned to measure the He-I $2^3S_1 \rightarrow 2^3P_{J=1,2}$ triplet transition. The central wavelengths for the transitions are $\lambda_{J=1} = 1083.025$ nm and $\lambda_{J=2} = 1083.034$ nm. The lines are scanned with a mode hop free tuning range of 10 GHz with a scanning frequency of 10 Hz. The beam passes through an orifice (b) and is split into three arms using a 20 mm thick quartz plate (c). The light of the detection arm passes an ND filter (d) to reduce power and to avoid saturation of the absorption signal and is then focused by a lens (e) on the centre of the optical arm of the DBD (f). The light is detected by a photodiode (g). The DBD is mounted on an xyz-stage, which allowed to scan through the discharge profile. The second arm of the laser light is guided to a Fabry-Pérot interferometer (h) with a free spectral range of 1 GHz. This allowed to convert the time axis of the laser scan into a frequency axis. In preliminary experiments the third arm of the laser beam was guided through a low pressure helium hollow cathode lamp (i), which served as reference for the position of the two optical transitions. The light from this arm was also detected by a photodiode (g). The metastable density is calculated by means of the Beer-Lambert law according to the method described by Korolov et. al [6].

OES setup. The temporally and spatially resolved OES measurements are performed in an end-on view of the discharge channel as illustrated by the sketch on the right side of the dotted box in Fig. 1. By means of a lens, the light is mapped on the chip of an ICCD-camera. The camera is externally gated by a function generator, which is synchronized with the frequency of the power supply for the discharge. This enables to temporally map the emission of the plasma during the discharge pulse. By inserting narrow bandpass filters in the optical path, spectral resolution can also be achieved. Optical filters for 391 nm, 706 nm and 777 nm were used to resolve spectral lines of N_2^+ , He and O, respectively.

3. Results and discussion

The results from the temporally and spatially resolved OES are depicted in Fig. 2. To achieve this representation, the emission intensities of the He, O and N_2^+ line within each ICCD image is normalized to its maximum and stacked in one graph. This allows to compare the propagation of the emission of different wavelengths directly in one graph. The thick black bars on the left side indicate the electrode positions.

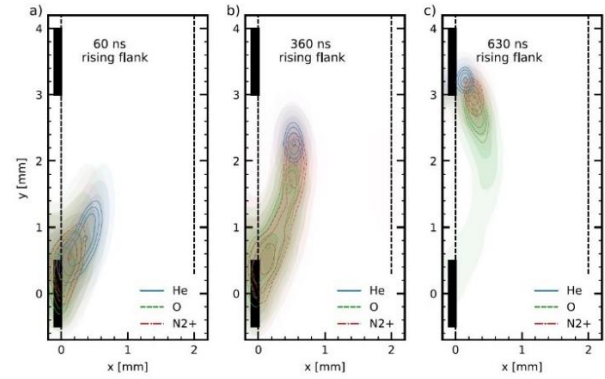


Fig. 2. End-on view of the propagation of the emission signal of He, O and N_2^+ at 60 ns, 360 ns and 630 ns

The emission from the discharge expands from the powered electrode to the grounded electrode. However, the position of the head of the emission wave of different species do not coincide for certain points in time. The signal from the N_2^+ line and the O line temporally follows the emission of helium. Moreover, in b) and c) the N_2^+ line and the O line show a tail, which is present over a longer period, whereas the emission from the He line is narrow and confined. These two observations indicate an involvement of helium metastables in the excitation of both N_2^+ and O in an afterglow-like process. At first, due to high electric fields helium metastables are formed in the tip of the emission wave. During the propagation of the wave, the remaining long living metastables collide with N_2 in Penning collisions forming N_2^+ , which leads to a delayed emission propagation of the N_2^+ emission forming a tail. A similar behaviour is valid for the O emission signal. O_2 needs to be dissociated and excited to be visible in emission. Also here, the He metastables are a candidate responsible for the dissociation of O leading to a delayed emission signal with a tail.

These results are comparable to observations made on the planar electrode design in previous studies, except for the bent structure. This indicates that properties of the basic discharge dynamics are transferable to the co-planar DBD. The OES measurement also shows that it was possible to geometrically force the plasma close to the walls and thus enhance the potential for removing analyte deposits from the glass wall.

By means of OES it is only possible to draw direct conclusions regarding the distribution of emitting excited species. However, the helium metastables as important collision partner responsible for the dissociation of the

analyte cannot be observed. Therefore, TDLAS is applied in order to quantify the metastable density within the plasma zone. The results from the TDLAS measurements are depicted in Fig. 3. The graphs result from scans along the y-axis at four different x-positions. For close distances to the glass surface of 0.4 and 0.7 mm, two maxima are visible corresponding to the foot points of the bent structure of the plasma. The highest metastable density is reached in the region of the powered electrode and is on the order of $4.5 \cdot 10^{13} \text{ cm}^{-3}$. In the region between the two electrodes the density drops by approximately a factor of two. With increasing distance from the glass surface in x-direction the maxima in the metastable density contract in y-direction. This corresponds to the bent structure of the plasma, which was observed by OES. Moreover, the highest metastable density is measured in front of the glass close to the electrode resulting in a high local potential for dissociation.

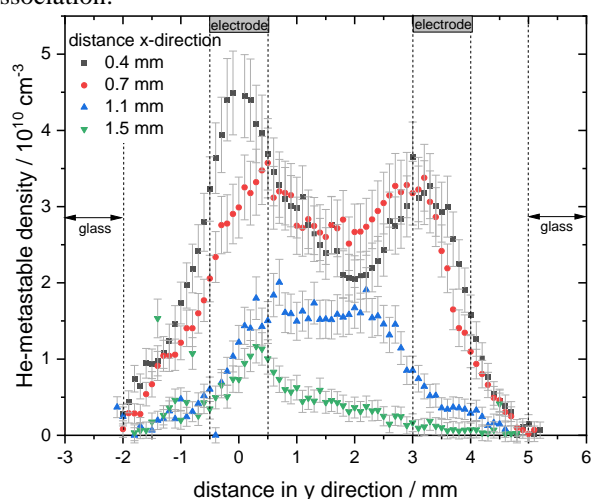


Fig. 3. Profiles of the helium metastable density obtained from scans in the y direction at different distances from the glass wall in x-direction.

4. Conclusions

A DBD with co-planar electrodes was designed, which forces a plasma in a bent structure close to the glass surface, thus potentially reducing analyte built-up on the wall. This was validated by temporally and spatially resolved OES. Moreover, by an additional spectral resolution enabled by multiple filters, which were introduced in front of the ICCD camera, differences in the propagation of the excitation wave in the plasma for the species investigated was shown. This behaviour corresponds to previous measurements conducted on common planar DBDs, which are used in analytical chemistry. Since previous studies showed that helium metastables play an important role in the dissociation of analyte molecules, it was essential to quantify the density of metastables in this discharge to around $4.5 \cdot 10^{13} \text{ cm}^{-3}$ at the footpoints of the bent structure. These results lay the foundation for understanding the discharge, which will in future work be applied under analytical conditions. Additionally, the estimation of the density of helium

metastables contributes to a comparability to other common discharge types in analytical chemistry.

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6. References

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