SPATIAL AND TEMPORAL DISTRIBUTION OF EXCITED Cl ATOMS IN A LINEAR DIELECTRIC BARRIER DISCHARGE *

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Abstract

This paper presents results on the spatial distribution of excited Cl atoms in a linear dielectric barrier discharge (DBD) at moderate pressure using diode laser atomic absorption spectrometry (DLAAS). A method based on the imaging of the collimated diode laser beam at relatively long distance from the plasma allowed to measure the relative density of the Cl metastable $^4P_{5/2}$ level with a spatial resolution in the discharge less than 100 µm. Comparative measurements were performed in an Ar as well as in a He plasma with small admixtures of CCl_2F_2. The highest density of excited Cl atoms is produced close to the temporary cathode in Ar and it is shifted towards the middle of the discharge in He for similar discharge conditions. These results are very important in improving the characteristics of a DBD detector applied in element selective detection of molecular species.

Introduction

In a recent publication [1] we reported on the application of a linear dielectric barrier discharge for diode laser atomic absorption spectrometry. Excited fluorine and chlorine atoms were measured at the dissociation of the halogenated molecules introduced in the discharge. Although the average gas temperature is close to room temperature and the power consumption is less than 1 W, the detection limits and the dissociation capability were comparable with those obtained in a microwave induced plasma.

In order to understand the mechanisms, which lead to a complete dissociation of molecular species, the discharge was investigated in respect with the internal plasma parameters like gas temperature and electron density. The gas temperature and electron density were derived from the excited Ar ($1s_4$-$2p_6$, 800.828 nm) line profiles spatially and temporally resolved taking into account all significant broadening mechanisms (Doppler broadening, pressure and Stark broadening). The results showed that only at the maximum of the current peak (around 11 µs after the beginning of the discharge cycle) and in the vicinity of the temporary cathode the gas temperature has a value of around 1000 K and the electron density is around $10^{15}/cm^3$. During the main time of the discharge cycle the gas temperature is close to room temperature and the electron density is much lower and cannot be calculated with the proposed method. This temporally and spatially very limited high electron density leads to the complete dissociation of the molecules introduced as analyte.

Taking into account the spatial distribution of excited atoms in the discharge, it is expected that the detection limit of Cl atoms will be improved if the measurements are

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* *This paper is dedicated to the 70th birthday of Dr. Geavit Musa and his significant contribution to the field of plasma physics and technology in the last 40 years.*

performed only in the plasma region where the excited atom density is maximum. These results will be presented below.

Experiment

The linear dielectric barrier discharge operating in Ar was investigated in detail elsewhere [2, 3] and the main properties derived from electrical and optical measurements where pointed out. It has to be underlined that the discharge has a transient behavior on every half period of the applied voltage with a current pulse width less than 20 µs. The excited species in the discharge follow this temporal behavior, the maximum of absorption signal being reached at 5-8 µs after the maximum of the current peak.

For the present investigations the discharge was operated in He or Ar with CCl_2F_2 admixture with a flow rate of 150 ml/min and a total pressure between 20 and 120 mbar. The measurements were performed at a frequency of 5 kHz and applied voltage of around 700 Vpp.

The excited Cl atoms on the metastable level were determined using the classical atomic absorption spectroscopy with a laser diode (Hitachi HL8325G) operating on the transition of Cl atoms at 837.824 nm ($^4P_{5/2} - {}^4D^o_{7/2}$).

The experimental arrangement for the measurements of the spatial distribution of the excited Cl atoms is shown in Fig 1. The collimated diode laser beam is passing the discharge channel of 50 mm length and 1 mm height and is then expanded by a convergent lens (f = 16 cm). A pinhole (500 µm) placed 1 m far away from the lens selects a small part of the transmitted laser beam representing a limited area in the plasma. The detection of the transmitted laser beam is performed by a fast Hamamatsu photomultiplier placed very close to the pinhole.

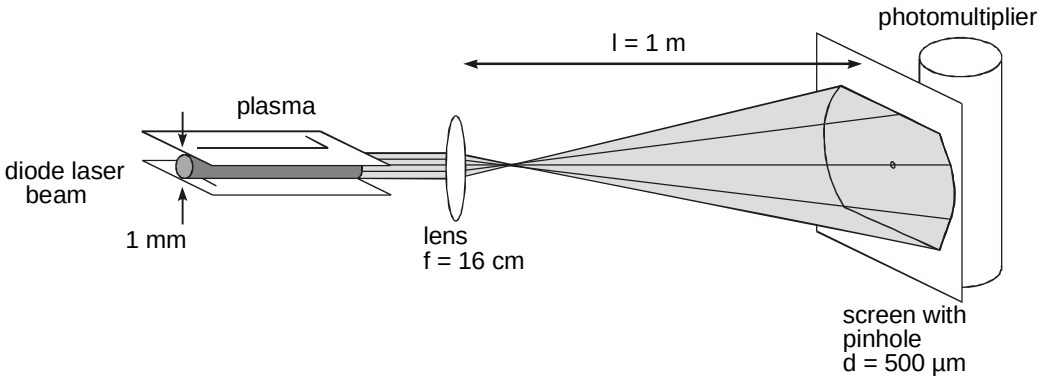

Fig. 1 Schematic view of the experimental arrangement
spatial resolution: 80 µm

Depending on the distance between lens and detector and the size of the pinhole, the resolution can be increased up to 40-50 µm without encountering diffraction problems. The absorption signals are measured on the whole period of the applied voltage allowing us to study also the temporal behavior of the excited species.

Distribution of Cl excited atoms on the $^4P_{5/2}$ level

The distribution of the excited Cl atoms on the metastable ($^4P_{5/2}$) level was measured in Ar with 150 ppm CCl_2F_2 for pressures between 20 and 50 mbar where the discharge presents an uniform working regime (glow type discharge). With higher pressures filaments start to be formed which can be easily observed in the shape of the current pulse. Measurements were also performed in He with 150 ppm CCl_2F_2 and the discharge is working stable up to 120 mbar.

The relative distribution of the excited Cl atoms for one period of the applied voltage in Ar as well as in He is presented in Fig. 2 for a total pressure of 40 mbar. From these measurements it can be seen that there is a difference between the absorption signal when Ar or He as carrier gas is used. In Ar the maximum density of excited Cl atoms is close to the temporary cathode, similar with previous results obtained only in the Ar plasma and this maximum is moving closer to the cathode with the increasing of the pressure [4] proving that the main part of energy is dissipated in a layer near to the cathode. The distribution of Cl atoms in He follows a totally different behavior. Most of the excited atoms on the metastable level are produced between the middle of the discharge and the anode. Only at much higher pressures the maximum is displaced in the direction of the cathode. Measurements of Ar excited atoms in an Ar/He mixture showed the same distribution like Cl/He mixtures.

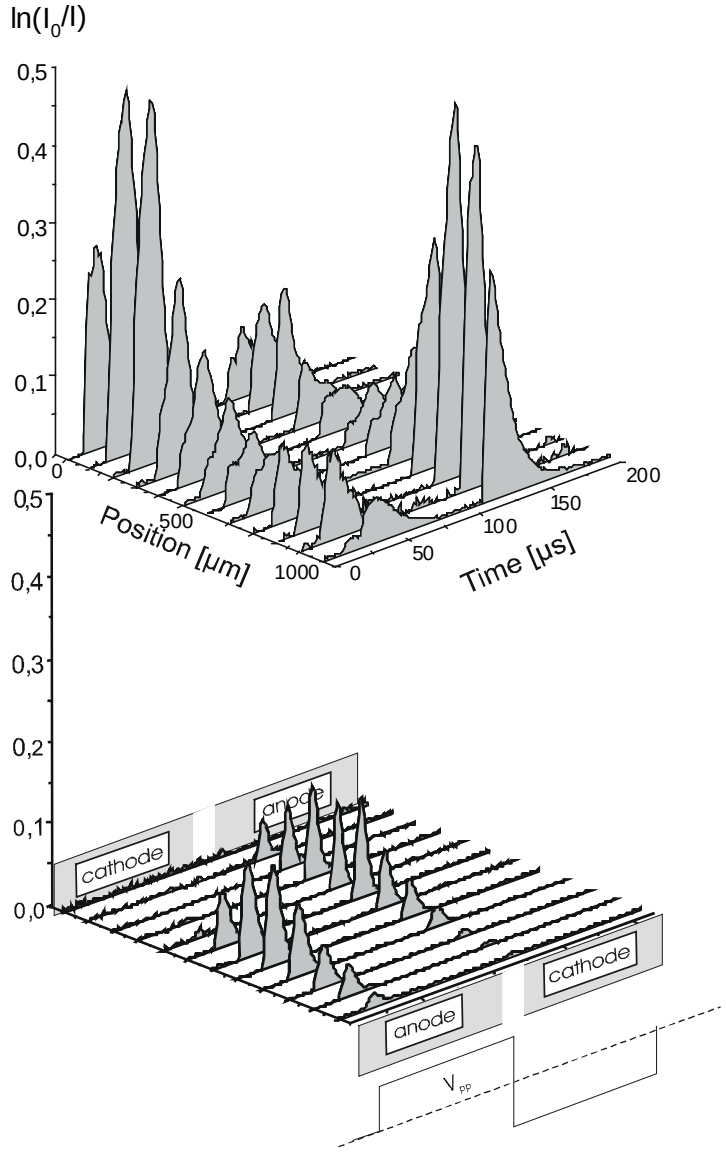

Fig.2 Spatial and temporal distribution of metastable Cl atoms in Ar (upper) and He (lower) for a total pressure of 40 mbar

The different distribution of excited Cl atoms in these two carrier gases can be explained taking into account the mechanisms of production of these excited atoms. The CCl_2F_2 molecule is dissociated in collision with the energetic electrons (complete dissociation energy around 16 eV) and Cl negative ions are formed. The electron detachment process followed by collisions with electrons and neutral atoms lead to the formation of Cl atoms in the ground and excited states.

There are few factors that generate different density distribution of the excited atoms between the electrodes. First of all the electron density in the He plasma is smaller than in Ar plasma at the same operating conditions. As a consequence there is a smaller density of excited Cl atoms in He (3 times smaller as it can be seen from Fig. 2) than in Ar due to the fact that electrons are mostly responsible for excitation. The metastable atoms of the buffer gas have also an important role in the feeding of the $^4P_{5/2}$ Cl level because they are a deposit of energy in the discharge. The first excited levels of Ar are laying less than 3 eV from the Cl $^4P_{5/2}$ level (around 9 eV) and collisional transfer between these levels resulting in the population of Cl level are very probable. In He the metastable levels are much higher (more than 19 eV) so Cl atoms cannot be excited on the metastable level through such a mechanism.

The displacement of the maximum density of Cl excited atoms can be explained by the value of the mean free path of the electrons which is in argon 3 times smaller than in helium[5] and the drift velocity of electrons which is in He 3-5 times higher [6] at the same reduced electric field. Electrons produced close to the cathode are moving further in a helium discharge than in an argon discharge. If we assume that Cl atoms are generated mostly due to collisions with electrons then the distribution of these excited atoms between anode and cathode is much broader in He than in Ar.

The temporal behavior is also different, the absorption signal of Cl excited atoms being narrower in He than in Ar. The excited atoms are decaying faster from the metastable level in the case of He proving that this level is mainly populated through electron collisions.

In the case of Ar as buffer gas, the absorption signal of Cl reaches another maximum at later times (later than 5 μs after the first maximum) and the formation time of this maximum depends on the position in the discharge. It is assumed that the second maximum is connected with the time dependent diffusion of the metastable atoms [7] produced in the negative glow of the discharge. This proves that Ar metastable atoms have a strong influence. Such behavior was not observed in the case of the He plasma.

Conclusions

The possibility to study the spatial distribution of excited atoms is an advantage for the measurements in small size discharges as well as for analytical spectroscopy where the detection limits have to be continuously improved. The different behavior of excited Cl atoms taken as a probe test of the discharge in respect with the filling buffer gas can give useful information about the discharge itself.

Taking into account the localized distribution of excited atoms, the detection limit of halogens is improved with one order of magnitude by absorption measurements performed in the limited volume containing the highest number density of excited atoms in the case of mixtures of the analyte with Ar and has almost the same value in the case of He.

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