

Low-pressure inductively coupled oxygen plasma loaded with acetone vapours studied by optical emission spectroscopy

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Abstract – Low-pressure inductively coupled oxygen plasma sustained within a linear glass tube was loaded by acetone vapours and characterized by means of the optical emission spectroscopy. Both spatial and temporal emission measurements were performed. Spectra consist mainly of the CO molecular bands which were used to characterize the plasma conditions. Spectral intensity of CO molecular band was studied versus partial acetone vapour and oxygen pressure.

1 INTRODUCTION

In the recent years interest for applications of low pressure inductively coupled oxygen plasmas is rapidly growing [1]. Applications are ranging from cleaning, surface modification to sterilization [2-6]. Acetone vapour plasma also has high potential in surface modification applications [7]. These increases the need for a rapid and simple method for plasma characterisation. Optical emission spectroscopy using versatile miniature fiber spectrometers appears as a widely applied technique [8-9]. It provides both spatial and temporal resolution and is applicable for real-time monitoring of plasma applications [10].

In the present work we have applied OES technique for characterisation of oxygen-acetone vapour mixture plasma emission. Combining oxygen and acetone (C_3H_5OH) could be important for extending plasma chemistry applications [11].

2 EXPERIMENTAL SETUP

The experimental setup is shown in figure 1. The discharge vessel was a linear tube with outer diameter of 4 cm made of a borosilicate glass which has a good transparency from 300 nm to IR [12]. The tube was connected to the vacuum system, which provides the pumping speed of 35 m³/h and the base pressure of 1 Pa. The total pressure in the system was measured with a Baratron gauge. Plasma was created within 8 turn coil connected through a matching network to a RF amplifier (RIZ SW Amp.). The amplifier was fed by oscillation from a frequency generator (Hameg HM8131-2) at a frequency of 13.56 MHz. The discharge power was adjustable up to 300 W. Forward

and reflected power component were monitored at the amplifier. The coil was placed at a distance of 5 cm from the edge of the glass tube ($z = 5$ cm) and its length was 14 cm. Acetone vapour was loaded into the discharge vessel through a capillary glass tube (outer diameter 0.6 cm, inner 0.1 cm). Acetone vapour pressure was regulated by a precise Teflon valve. Glass vessel that contains pure acetone was kept at the room temperature. Diameter of capillary tube exit was about 0.03 cm. Oxygen gas was added into the plasma through separate needle, and the flow measured by a mechanical flow meter.

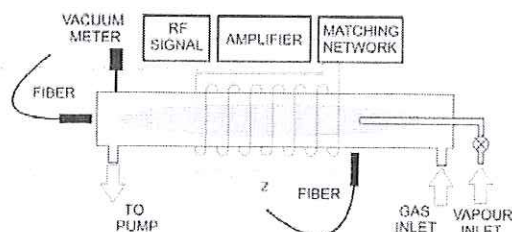


Figure 1: The experimental setup

The emission was observed both perpendicularly to the plasma tube and through the whole plasma column. Perpendicular measurements were performed by means of a LIBS2000+ spectrometer system from Ocean Optics which consists of seven miniature spectrometers. The nominal spectral resolution was 0.1 nm in the spectral range from 200-980 nm. Each spectrometer is equipped with Sony CCD array (2048 pixels and 12 bit A/D conversion) used as a detector. Longitudinal observation was made simultaneously by means of HR-2000 – UVVIS broad band spectrometer having spectral resolution of 1 nm. The spectral response of spectrometers was determined by means of a combined deuterium tungsten reference light

source. It was important to perform spectral response calibration for each integration time of the CCD spectrometer. Spectrometers were controlled, and saved spectra analyzed by homemade software developed within the LabVIEW. Simultaneously plasma images were recorded by a standard CCD camera for each set of gas pressures and discharge power parameter. The light was collected by means of an optical fibre perpendicularly to the plasma tube. Optical fibre contains seven distinct fibres and a lens with a divergence angle of 2° . The distance from the collecting lens to the tube wall was 0.4 cm. The fibre was moved in steps of 1 cm along the tube (40 cm effective length). At each position spectra were recorded for 10 seconds with integration times up to 2 seconds, and then averaged.

3 RESULTS AND DISCUSSION

Figure 2 shows optical emission spectra in the region from 200 nm to 1000 nm of pure acetone vapour plasma at different acetone vapour pressures. The applied plasma power was 150 W. Spectra were observed through the plasma column longitudinally.

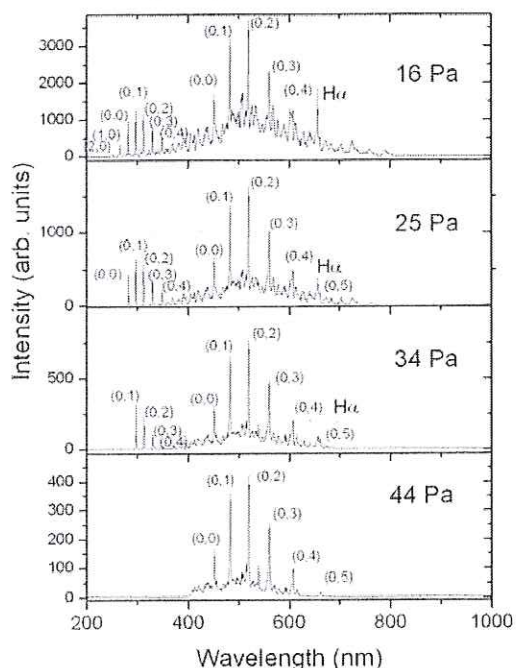


Figure 2: Characteristic spectra of acetone vapour plasma for different acetone vapour pressures at constant applied power of 150 W.

Two prominent CO molecular bands were identified. The Angstrom band (450-700 nm region) and 3rd

positive band (260- 400 nm region). They correspond to the $B^1\Sigma^+-A^1\Pi$ and $b^3\Sigma^+-a^3\Pi$ electronic transitions of the CO molecule, respectively. In addition, region of the Angstrom band is spectrally overlapped with structured continuum which extends from 300 nm to 800 nm. The most probably it originates from the chemiluminescence resulting from the radiative combination of atomic oxygen and carbon monoxide which form the CO₂ molecule [13]. The spectra shown in figure 2 were not corrected to the spectral response. This was performed when spectral intensities of different atoms or molecules were compared to each other. The spectra response is changing substantially in UV (below 400 nm) and IR (above 800 nm).

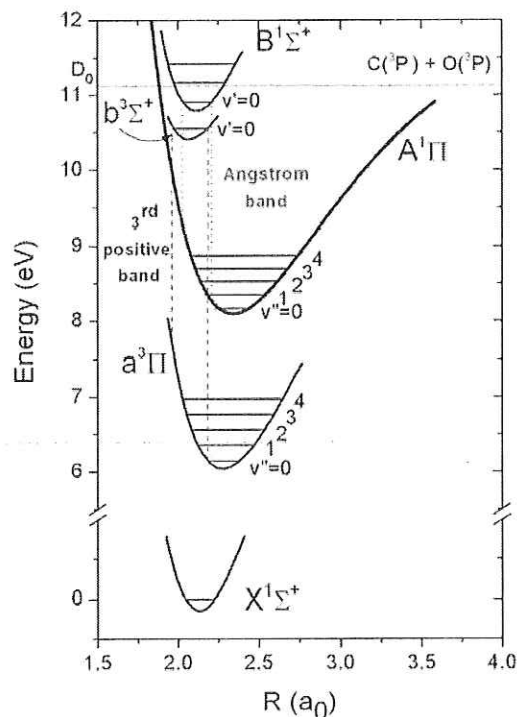


Figure 3: The relevant partial potential energy curve diagram of CO molecule. The sampling regions of vibrational energy levels within the electronic ground states are indicated with vertical dashed lines.

An interesting feature was observed as acetone vapour pressure is changing. Starting with higher pressure at given applied discharge power of 150 W only Angstrom band of the CO was observed. Eventual emission in UV is below the threshold of CCD detector with 500 msec integration time. As acetone vapour pressure decreases spectrum extends towards UV and the 3rd positive band appears. At the

lowest pressure vibrational transitions from ($v' = 2$) could be observed. As pressure decreases the electron density and temperature of the plasma increase which results with the population of higher vibrational energy levels of the relevant electronic states due to collisions of CO molecules with electrons. Note that as pressure decreases hydrogen atomic emission appears. The wider portion of spectrum can then be understood in terms of the Mulliken difference potential [14]. The concept of Mulliken difference potential states that during electronic transition not only internuclear distance is conserved but also the kinetic energy. The relevant potential energy diagram is shown in figure 3. The vertical dashed lines are drawn from the turning point of specific vibrational level of the upper electronic state to indicate the region of vibrational levels within the lower electronic state to which the emission is possible. As higher vibrational levels of the upper electronic state are populated this sampling region gets wider and additional vibrational bands appear in spectrum. We have observed similar spectral behaviour for fixed acetone vapour pressure by increasing the applied discharge power. Therefore we believe that CO molecular band emission could be used as a good sensitive marker of the plasma conditions provided the full spectral simulation is performed [15].

When oxygen gas is added to acetone plasma spectrum changes in the sense that hydrogen atomic emission increases and in addition the OH molecular band at 309 nm appears. Typical signature of oxygen presence through atomic line emission appears as well depending on relative ratio of oxygen gas and acetone vapour pressure. The oxygen lines at 777.2 nm and 844.4 nm were the most prominent.

In the second set of measurements spectra were observed at a given fibre position near the capillary tube exit and discharge power while acetone vapour pressure was varied. This change was specifically connected with opening and closing of the TEFLON valve. Typical time sequence is shown in figure 4.

At the top of figure 4 change of the total pressure (oxygen and acetone vapour pressure) is shown as measured by the Baratron in comparison to typical spectral behaviour of the CO (0,2) 519.3 nm, H α (656.2 nm), O (777 nm) and OH (309 nm). Dashed lines in figure 4 indicate the opening of the acetone vapour valve (approximately 20 s after plasma activation under initial oxygen pressure of 30 Pa) and closing of the acetone vapour valve (approximately 35 s after plasma activation). Valve is completely open within 2-3 s. Following the opening of the valve, pressure rises to the given value after 10 s. Pressure was at the maximal value for another 10 s. When the valve is closed pressure drops to the initial oxygen pressure, although somewhat slower than during the

rise of pressure. Spectral intensities of different lines show interesting behaviour, opening of the valve leads to an immediate increase in intensities of all lines (except oxygen), followed by decrease to a constant value until the valve is closed. After the closing of the valve intensities of atomic lines show a large increase and afterwards a steady decrease.

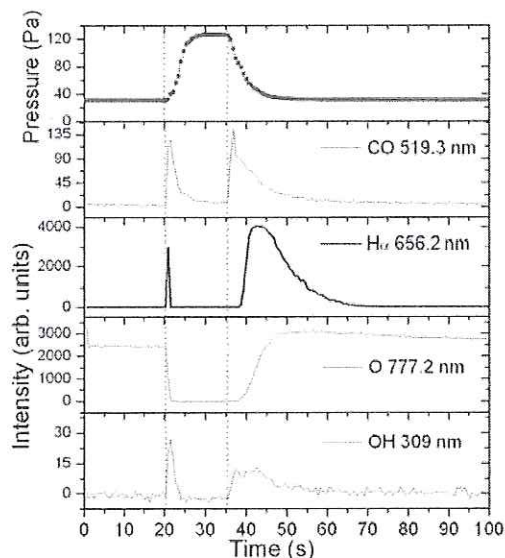


Figure 4: Time sequence of the spectral intensities during loading and removing of acetone vapour from oxygen plasma. The applied discharge power was 150 W and spectrometer integration time 500 ms.

We note that upon opening the valve for acetone vapour, sudden decrease of oxygen emission is connected with sharp intensity peak of OH, H, and CO. When partial acetone vapour pressure achieves the maximum of about 90 Pa only weak emission was observed from the plasma. The oxygen is consumed for chemical reactions with CO, H and OH. Obviously product(s) of these reactions does not emit UV or visible light. However, one should keep in mind that as total pressure increases less energetic electrons are available and therefore excitation by electron collisions gets weaker. This can be recognized also from the CO emission changes as shown in figure 2. As partial acetone vapour pressure decreases fast CO and OH intensity increase was observed while H and O atom emission recovers with some delay about 5 seconds. During the process of cleaning of plasma and discharge vessel a big amount of hydrogen is released. We believe that more detailed examination of transition behaviour could give important information on plasma chemistry which is behind. In addition to the above mentioned features we mention that degassing of

acetone vapour into plasma under certain conditions induces various striation phenomena such as plasma slices and deposition of the back coating on the plasma tube, which are investigated separately [12].

4 CONCLUSIONS

The low pressure oxygen-acetone vapour mixture plasma has been characterized by means of optical emission spectroscopy. Dominantly observed CO molecular band emission in pure acetone plasma was found particularly sensitive on plasma conditions. The presence of oxygen in plasma reduces cleaning time after the acetone vapour degassing into the discharge vessel is stopped comparing to the case of pure acetone vapour plasma. Interplay of spectral intensities of main plasma constituents can be used for plasma modeling.

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