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REFERENCE: Short Term Scientific Mission, COST CM0601

Beneficiary: Jan SKALNY, Comenius University Bratislava

Host: Prof. Nigel J. Mason, Open University UK

Period: from 06/04/2008 to 12/04/2008 Place: Milton Keynes and Warington UK

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SCIENTIFIC REPORT

PURPOSE OF VISIT

There is long years existing collaboration between open University and the Department of Experimental physics, Comenius University, Bratislava. Number of papers has been published during that period. The aim of the present STSM is to study the mass spectra of ions produced by corona discharge. We plan to use the corona discharge within the ECCL project for formation of thin films on metals and on semiconductors, especially SiO₂ films. The advantage of this method is high pressure in the plasmachemical reactor. The process of deposits formation is very complex and both neutral species as well as the ions and electrons take are active in this process. According our knowledge there is a lack of information about the ions produced in such discharges. The same can

be concluded in case of neutral species. Therefore there is need to know more about both of mentioned two groups of species. We would like to use the newly developed and constructed high pressure mass spectrometer produced by Hiden comp. The plasmachemical reactor based on corona discharge has been designed and manufactured in laboratories in Bratislava. This will be used in experiments. The experiments will be performed in collaboration with Open University, especially with doctoral students of Prof. Nigel Mason. The mass spectra of ions produced by DC corona discharges of both polarities initiated in oxygen, air and carbon dioxide will be studied at various working conditions in the discharge. The results will be compared with surface analysis of plane electrode on which the deposits is formed. The analysis will be done in laboratories in Bratislava.

DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT

The plan of activities has been fullfiled. The newly developed corona discharge reactor, constructed in Bratislava has been jointed with mass spectrometer fy. Hiden from Warington. Exeperiments have been performed in laboratories of mentioned company. The aim of experiment was the study of effect of humidity on specrs of positive and negative corona discharge in air and oxygen. During the stay I have finished number of experiments. Results will be analyzed in laboratories in Baratislava. Some of them will be prepared soon as abstract for international conferences.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Positive corona. The mass spectra of positive ions were measured at constant distance between electrodes of 6 mm. Only the cluster ions H_3O^+ . $(H_2O)_n$ were appeared in the spectrum. The relative yield of minor ions was below 1% at all three discharge currents 10, 25, and 50 μ A. Surprisingly the relative yields of individual clusters ions were not affected by the discharge. The small changes can be ascribed to inaccuracy of measurement. The maximum relative yield of 43 % has been found at n = 4. With increase in n the relative yield was decreasing up to 2 % at n = 10. There are two primary ions O_2^+ and N_2^+ formed in glow region of positive corona discharge in air near the point electrode. The ions N_2^+ undergo fast ion-molecule conversion

$$N_2^+ + O_2 \to O_2^+ + N_2 \tag{1}$$

The ions O_2^+ react with water molecules

$$O_2^+ + H_2O + M \to O_2^+ \cdot H_2O + M$$
 (2)

The ions O_2^+ . H_2O are converted to oxonium ions H_3O^+ via process

$$O_2^+ H_2 O + H_2 O \to H_3 O^+ + OH + O_2$$
 (3)

The ion H_3O^+ is the first member of group of clusters $H^+(H_2O)_n$ n = (1, 2,...), which are formed in sequential reactions

$$H_3O^+.(H_2O)_n + H_2O + M \to H_3O^+.(H_2O)_{n+1} + M$$
 (4)

Negative corona. There are two primary negative ions formed in negative corona discharge in air. First one is O⁻, which is produced only in glow region via dissociative electron attachment

$$e + O_2 \to O^- + O \tag{5}$$

Contrary to previous one, the ion O_2^- is formed predominately in drift region where the reduced electric field is low. The three body collisions is the formation process

$$e + O_2 + M \to O_2^- + M \tag{6}$$

The ions O⁻ are either converted to CO₃⁻ via

$$O^{-} + CO_2 + M \to CO_3^{-} + M \tag{7}$$

or to O3⁻ via

$$O' + O_2 + M \to O_3^- + M$$
 (8)

Both CO_3^- and O_3^- form in collisions with water molecules clusters CO_3^- . $(H_2O)_n$ and O_3^- . $(H_2O)_n$. The mentioned clusters were observed in spectra. The ions O_2^- are the source of clusters O_2^- . $(H_2O)_n$

$$O_2^{-} + H_2O + M \to O_2^{-} \cdot H_2O + M$$
 (9)

The relative yield of O_2^{-} .(H₂O)_n cluster ions is considerably decreasing with increasing distance between electrodes because of active process

$$O_2^-(H_2O)_n + NO_2 \to NO_2^-(H_2O)_{n-1} + O_2 + H_2O$$
 (10)

The abundance of NO_2^{-} .(H₂O)_n clusters was found to be low but increased with increasing distance between the electrodes. The fastest process responsible for depletion of O_2^{-} ions and theirs clusters is conversion of O_2^{-} to O_3^{-}

$$O_2^- + O_3 \to O_3^- + O_2 \tag{11}$$

The process (11) can be also active if ions are in cluster form. Besides of clusters mentions above also the clusters $NO_3^{-}.(H_2O)_n$, $NO_3^{-}.HNO_3$, and $HCO_3^{-}.(H_2O)_n$ were observed in ion spectra. The ions $NO_3^{-}.(H_2O)_n$ are produced via charge

$$CO_{3}^{-}.(H_{2}O)_{n} + NO_{2} \rightarrow NO_{3}^{-}.(H_{2}O)_{n} + O_{2}$$
 (12)

The relative yield of NO_3^{-} .(H₂O)_n is increasing with increasing distance between electrodes.

FUTURE COLLABORATION WITH HOST INSTITUTIONS

Collaboration will be lasted in next mothts when one student will continue started experiments. Analysis of results will be performed in Bratislava. The construction plans of new reactor will be completed and reactor will be manufactured in near future in Bratislava. This will be used both in Bratislava and at Open University

PROJECTED PUBLICATIONS/ARTICLES RESULTING OR TO RESULT FROM THE STSM

During the STSM abstracts and extended abstracts for international conferences have been prepared

1. The effect of humidity on the properties of DC positive and negative corona discharges fed by Air and Oxygen: Ozone generation in dry and wet gases.

J. D. Skalný, J. Országh, Š. Matejčík and N. J. Mason Paper will be presented at conference STPP Praguje, June 2008

2. Mass Spectrometric Analysis of Ions Formed in Air-fed Corona Discharges

J. D. Skalny

Contribution has been presented as Invited lecture at EU-Japan conference.

Jan Skalny

Bratislava 30 April, 2008.

CONFIRMATION BY THE HOST INSTITUTE OF THE SUCCESSFUL EXECUTION OF THE MISSION

The visit of Prof. Jan Skalny was underdone with success and in accordance with the planed activities.

Prof. Nigel J. Mason

Milton Keynes, 30 April 2008