IPS 2012

5th International Workshop on Plasma Spectroscopy

Presqu'île de Giens
13-16th May 2012

Laboratoire de Physique des Plasmas
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IPS 2012 WORKSHOP PROGRAM

Session 1: Monday 14th, 9h00

1) **Invited Lecture:** *G.A.D. Ritchie* - Coherent spectroscopy with quantum cascade lasers
2) *D. Marinov* - Surface vibrational relaxation of N2 studied by infrared titration with time resolved Quantum Cascade Laser diagnostics
3) *V.L. Kasiutsich presented by P.A. Martin* - Infrared laser spectroscopy of molecular hydrogen

--*Coffee break*--

4) *N. Lang* - The potential of quantum cascade laser absorption spectroscopy for plasma technological applications in industry
5) *G. D. Stancu* - Studies of carbon monoxide emission using Mid-IR QCLAS in methane flames stabilized by nanosecond pulsed discharges
6) *S. Welzel* - Infrared gas phase studies in high-current dielectric barrier discharges containing organo-silicon precursors

Session 2: Monday 14th, 16h00

1) *R. Martini* - Optically modulated Quantum Cascade Laser - progress towards a frequency comb in the MIR
2) *V.I. Zaitsev* - X-ray Spectroscopy of the Megaamper Z-pinches
3) *T. Dandl* - Light Emission from Rare Gases using Combined Electron-Beam and Radio-Frequency Excitation

Poster session and industrial exhibition: Monday 14th, 17h30

--*Coffee break*--

4) *Y.Abe presented by K. Takeda* - Measurement of the flux ratio of hydrogen atom to film precursor for microcrystalline silicon solar cell
5) *C. Barakat* - Adsorbed phase and gas phase study of isopropanol oxidation by ozone on TiO$_2$ for surface regeneration
6) *G. Bourgeois* - Time-resolved LIF measurements in a low pressure magnetized DC discharge
7) *A. Brablec* - OES diagnostics of underwater diaphragm discharge generated by HV pulses at atmospheric pressure
8) *F. Brehmer presented by S. Welzel* - Dissociation study on CO$_2$ in an atmospheric pressure plasma
9) *R. Chodun* - Atomic Emission Spectroscopy – the tool of optimization of the aluminium nitride thin films synthesis by reactive magnetron sputtering method for electronics applications
10) *L. Dosoudilova presented by A. Brablec* - Comparison of methods of self-absorption and effective branching fractions for metastable densities determination in surface-wave neon plasma
11) *E. Fasci* - QCL-Optical FeedBack Cavity Enhanced Spectrometer for real time monitoring of Formaldehyde: application to air plasma treatment system
12) *Z. Gavare* - Studies of self-modulation phenomena in high-frequency electrodeless lamps
13) *A. Gómez presented by H. Martínez* - Optical emission spectroscopy for diagnostic and monitoring of O2 plasma used for modifications of tin sulphide thin films
14) *F. Hempel* - On investigations of the reaction kinetics in dust producing rf discharges in gas-mixtures of Argon or Helium and hydrocarbons
15) *Mr Hrycak* - Spectroscopic measurements in plasma generated by waveguide-supplied coaxial-line-based nozzleless microwave source
16) *D. Lopatik* - On application of cw external-cavity quantum cascade infrared lasers for plasma diagnostics
17) *D. Marinov* - Ozone production in O$_2$ plasma at low pressure: evaluation of surface and gas phase mechanisms
18) *V. Mazankova* - Study of the barrier discharge in argon/acetylene mixture

19) V. Mazankova - Power dependence of the nitrogen pink afterglow effect
20) *S. Muthmann* - The response of microcrystalline film growth to changing plasma conditions observed by optical emission and in-situ Raman spectroscopy
21) A. Nikiforov - On laser induced spectroscopy of OH radical applied to an atmospheric RF plasma jet
22) *P.G Reyes* - Optical emission spectroscopy of H_α and H_β in a glow discharge mixture of Ar/H_2
23) *A. Svagere* - Intensity changes in time of high-frequency electrodeless discharge lamps containing heavy metals
24) *F. Thevenet* - Combination of FTIR spectroscopy and GC-FID+MS to elucidate toluene reactivity induced by non-thermal plasma at ppb levels
25) J. Voráč - Measurement of OH concentration by laser-induced fluorescence in an atmospheric RF plasma jet
26) S. Welzel - Infrared gas phase studies in air-like atmospheric pressure DBDs

Session 3: Tuesday 15th, 9h00

27) **Invited Lecture:** *O. Axner* - NICE-OHMS - A Frequency Modulated Cavity Enhanced Spectroscopic Technique for Detection of Gases down to the 10^{-12} cm^{-1} $Hz^{-1/2}$ Range
28) *A.F.H. Van Gessel* - Gas temperature and NO density measurements in atmospheric pressure plasmas
29) *K. Takeda* - Diagnostics of Atomic Oxygen in O2/Rare Gas Mixture Plasma with Vacuum Ultraviolet Laser Absorption Spectroscopy

--*Coffee break*--

30) *I. Marinov* - Time-resolved optical emission spectra of nanosecond discharge in water
31) *D. Hegemann* - Plasma chemical gas phase processes in plasma polymerization
32) *M. Cirisan* - Study of the optical thickness of laser induced plasma for improved material analysis via laser-induced breakdown spectroscopy

Session 4: Tuesday 15th, 16h00

33) **Invited Lecture:** *D. Romanini* - Cavity enhanced with optical feedback using QCL lasers: Trace analysis at ppt levels in the mid-infrared range
34) *M. Hübner* - Quantum Cascade Laser Absorption Spectroscopy (QCLAS) applied for a temperature study of low pressure pulsed dc plasmas
35) *J. Winter* - Detection of ozone in an atmospheric pressure plasma jet

--*Coffee break*--

36) *M. Rivallan presented by F. Thibault-Starzyk* - In situ and operando FT-IR spectroscopy for plasma in catalysis
37) *S. Loganathan* - Plasma Regeneration of TiO2 Surface Saturated by IPA: Influence of Air Relative Humidity
38) *S. Ponduri presented by S. Welzel* - Plasma-assisted CO_2 reduction in synthetic fuel processing

Session 5: Wednesday 16th, 9h00

39) M. Aldén - Probing combustion and other harsh environments using laser spectroscopic techniques
40) J.P. Booth - Chlorine atom and molecule dynamics in an inductively coupled plasma in pure Cl_2
41) M. Carras - InP Based QCL for spectroscopy at III-V Lab

--*Coffee break*--

42) *H. Hildebrant presented by S. Stepanov* - The Use of Optical Emission Spectroscopy for Inline Monitoring of the Atmospheric Pressure Plasma Pre-treatment Process in Adhesive Bonding Technology
43) *S. Mitic* - Particle Characterization by means of White Light Scattering

SESSION 1

Monday 14th, 9h00

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Coherent spectroscopy with quantum cascade lasers

Grant A.D Ritchie

Department of Chemistry , The Physical & Theoretical Chemistry Laboratory,
The University of Oxford, South Parks Road, Oxford, UK E-mail: grant.ritchie@chem.ox.ac.uk

High power single mode quantum cascade lasers (QCLs) open up the possibility for rovibrational state preparation of gas phase molecules in low frequency vibrational modes. Examples of pump and probe experiments with cw QCLs with these aims will be presented.

Recently we have used two 5 µm cw QCLs to perform a counter-propagating pump and probe experiment on a low pressure sample of nitric oxide [1]. The strong pump field excites a fundamental rovibrational transition and the weaker probe field is tuned to an appropriate rotationally resolved hot band transition. When both light fields are in resonance, rapid passage is observed in the hot band absorption lineshape arising from a minimally damped and velocity-selected sample of molecules in the v = 1 state.

In these first experiments a commercial external cavity QCL (140 mW power, linewidth = 2 MHz Daylight Solutions) was used as the pump laser while the probe laser was a distributed feedback QCL (7 mW, linewidth = 16 MHz, Alpes Lasers). Most recently, the weak probe has been replaced with a higher powered (up to 190 mW) narrow bandwidth (800 kHz) device. Figure 1 adjacent shows example data obtained with 35 mTorr of NO in a 70 cm long cell in which the $R(14.5)_{1/2}$ v = 1←0 and $R(15.5)_{1/2}$ v = 2←1 transitions are used as the pump and probe transitions respectively. In these experiments, the pump and probe powers were 80 mW and 41 mW respectively and their chirp rates were 150 Hz ns^{-1} and 145 KHz ns^{-1}. The data clearly shows the effect of rapid passage as the probe interrogates a velocity selected vibrationally excited sample.

The rapid passage structure is well fit by a (exponentially) damped sinusoidal function and the fitted decay constants, τ, are a function of the total sample pressure – see figure 2. As expected the rapid passage signal decays more rapidly with increasing pressure of NO as the increased collision frequency leads to more rapid dephasing and relaxation of the induced polarisation. It is also noted that the decay constants are subtly different for each Λ doublet of the pumped rotational state indicating that the underlying hyperfine structure of the transition plays a role in determining the dephasing of the observed signals.

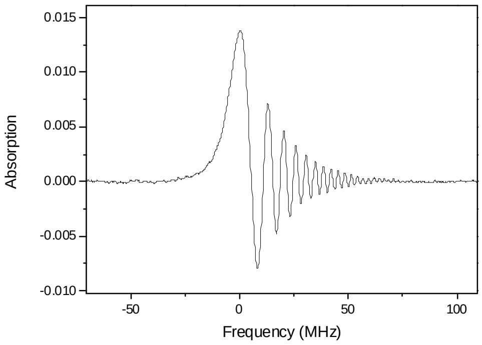

Fig. 1: *An example of the velocity selected hot band transition lineshape observed when pumping NO on a fundamental ro-vibrational transition.*

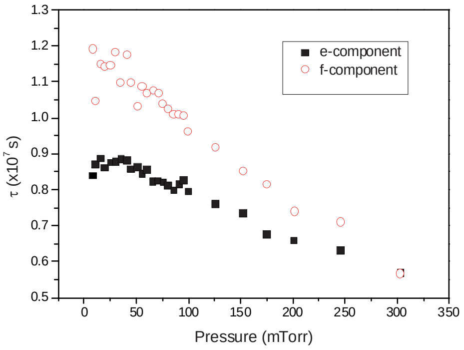

Fig. 2: *Measured decay constants for each of the velocity selected Λ doublets prepared in v = 1.*

References

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Surface vibrational relaxation of N_2 studied by infrared titration with time resolved Quantum Cascade Laser diagnostics

D Marinov[1,2], D Lopatik[3], O Guaitella[1], M Hübner[3], Y Ionikh[2], J Röpcke[3] and A Rousseau[1]

[1]*LPP, Ecole Polytechnique-91128 Palaiseau, France E-mail: daniil.marinov@lpp.polytechnique.fr*
[2]*St Petersburg State University, Institute of Physics, Ulianovskaya 1, 198904 St Petersburg, Russia*
[3]*INP Greifswald, Felix-Hausdorff-Str, 17489 Greifswald , Germany*

A new method for determination of the de-excitation probability γ_{N2} of vibrationally excited N_2 on different surfaces has been developed. A short DC discharge pulse was applied to a mixture containing 0.05-1% of CO_2, N_2O or CO in N_2. In the afterglow, the vibrational relaxation of titrating molecules was monitored *in-situ* using quantum cascade laser absorption spectroscopy (QCLAS). The experimental results were interpreted in terms of a numerical model of non-equilibrium vibrational kinetics.

1. Introduction

In nitrogen containing plasmas, vibrationally excited $N_2(v)$ acts as an energy reservoir that affects electron kinetics, chemistry and thermodynamic properties of the plasma. In bounded low pressure laboratory plasmas, relaxation on the reactor walls is the most efficient $N_2(v)$ loss mechanism. Therefore, the knowledge of the heterogeneous deactivation probability of $N_2(v)$ (γ_{N2}) is crucial for plasma modeling. The development of a simple and reliable technique for *in-situ* γ_{N2} determination based on the titration with IR active molecules [1,2] was therefore the main motivation of the present study.

2. Experimental

Gas mixtures containing 0.05-1 % of titrating molecules (CO_2, N_2O, CO) in N_2 were excited by a single DC discharge pulse (I=50 mA, τ=1-10 ms) at a pressure of 133 Pa. The relaxation kinetics of CO_2 (N_2O, CO) was followed using a 3-channel quantum cascade laser (QCL) spectrometer TRIPLE Q [3] with time resolution up to 10 µs. Experiments were done in a single pulse mode without accumulation.

Due to a very efficient vibrational coupling between N_2 and CO_2 (N_2O, CO), the excitation of titrating molecules reflects the degree of vibrational excitation of N_2.A model of vibrational kinetics in N_2 with CO_2 (N_2O, CO) admixtures was developed and the value of γ_{N2} was determined from the best agreement between the model and the experiment.

3. Results

With laser absorption spectroscopy a combination $(N_0 - \beta N_1)$ of the populations of the lower ($[CO_2(00^00)] \equiv N_0$) and the upper ($[CO_2(00^01)] \equiv N_1$) vibrational levels is actually measured. Figure 1 shows the time evolution of $(N_0 - \beta N_1)$ in a silica discharge tube for different initial concentration of CO_2. One can see a depletion of the measured value of $(N_0 - \beta N_1)$ due to the vibrational excitation of CO_2 upon the application of the discharge pulse. Vibrational relaxation takes place in the afterglow, the difference between the CO_2 concentrations before the pulse and when the relaxation is finished is ascribed to the dissociation of CO_2 in the discharge. The result of the modeling for 0.2% CO_2 is shown on the same graph, the relative uncertainty of γ_{N2} determination by fitting procedure was estimated to be 15%.

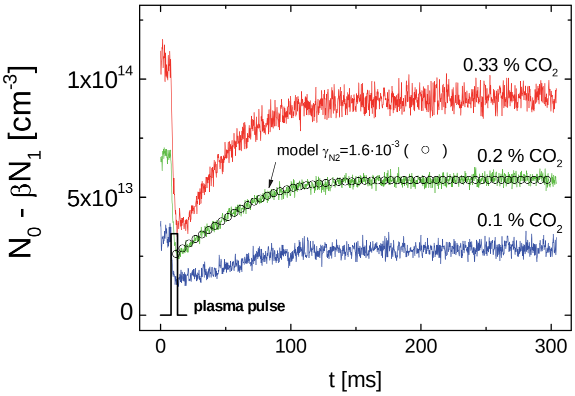

Fig. 1: Time evolution of $(N_0 - \beta N_1)$ after a I=50 mA, τ=5 ms pulse in silica discharge tube.

It was found that the value of γ_{N2} depends on the partial pressure of titrating molecules, what suggests a vibrational energy transfer mechanism between $N_2(v)$ and physisorbed CO_2 (N_2O, CO). Using the described technique the value of γ_{N2} was determined for SiO_2, TiO_2, Al_2O_3, Pyrex and anodized aluminium. The effect of plasma exposure on the efficiency of vibrational $N_2(v)$ quenching on different materials was observed and studied for reactive (N_2, O_2) and non-reactive (Ar) plasma pre-treatments.

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Infrared laser spectroscopy of molecular hydrogen

V.L. Kasiutsich[1], E.D. Mcnaghten[2], P.A. Martin[1]

[1]*School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M13 9JP, UK*
E-mail: philip.martin@manchester.ac.uk
[2]*AWE, Aldermaston, Reading, RG7 4PR, UK*

Off-axis cavity-enhanced absorption spectroscopy has been used to measure the S(1) quadrupole band of the fundamental 1 – 0 vibrational band of molecular hydrogen for applications in plasma catalysis.

1. Introduction

Plasma catalysis is one approach to produce molecular hydrogen from CH_4 for a range of applications in the energy sectors such as fuel cells. In order to study these processes in detail a direct optical method for quantitatively measuring hydrogen is required. Infrared laser spectroscopy is often used for measuring low concentrations of trace gases but hydrogen does not exhibit electric dipole moment transitions in the infrared spectral region. However it does possess a weak quadrupole moment which can be used if long optical absorption pathlengths are employed. This work describes an off-axis cavity-enhanced absorption experiment to measure hydrogen around 2.1 μm.

2. Methodology

2.1. Theory

Quadrupole transitions have the rotational selection rule $\Delta J = 0, \pm 2$ which gives rise to a Q branch as well as S and O branches. The quadrupole moment spectrum of H_2 was first measured by Herzberg in 1949 [1] and later by Fink et al. [2]. The S(1) line of the fundamental vibrational quadrupole band has a linestrength of 3.36 x 10^{-26} cm/molecule at 298 K.

2.2. Experimental

A cw-DFB diode laser producing around 5 mW at 2122 nm was used to illuminate a high finesse optical cavity of length 19.4 cm in an off-axis alignment. The laser light emerging from the cavity was focused onto an extended InGaAs photodetector. Difficulties were encountered due to amplified spontaneous emission of the laser passing through the cavity onto the detector.

Hydrogen gas (99.99%) was introduced into the optical cavity using a gas sample bag and the infrared spectrum at several different pressures was measured.

3. Results and Conclusions

Figure 1 shows an example of the spectra obtained with the off-axis cavity enhanced absorption technique. The very low laser power detected at exit of the cavity limited the detection limit to 0.16% hydrogen for 200 scan averages within 2 s. This was limited by detector noise. Higher laser power and a longer effective pathlength should enable detection limits lower than ppm levels.

In conclusion, we have demonstrated that off-axis cavity enhanced absorption spectroscopy can be used to quantitatively measure molecular hydrogen in the infrared spectral range. The technique can now be incorporated into the atmospheric pressure plasma catalysis reactor to study the formation of hydrogen.

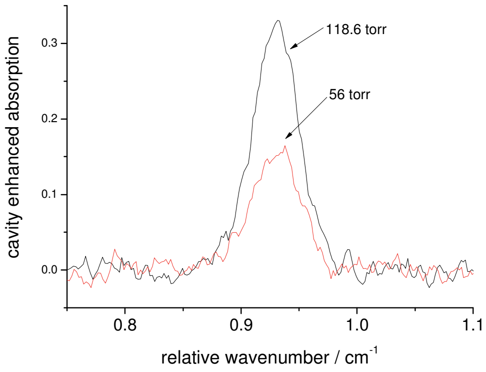

Fig. 1: *Cavity-enhanced absorption spectrum of the S(1) quadrupole transition 1 – 0 on H_2 at 4712.89 cm^{-1} (2122 nm) for different pressures of H_2.*

References

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[2] U. Fink, T.A.Wiggins, D.H.Rank: J.Mol. Spec 18, (1965) 384.

The potential of quantum cascade laser absorption spectroscopy for plasma technological applications in industry

N. Lang[1], H. Zimmermann[1], U. Macherius[1], J. Röpcke[1]

[1]*INP Greifswald, Felix-Hausdorff-Str, 17489 Greifswald , Germany E-mail: lang@inp-greifswald.de*

Recent applications of infrared absorption spectroscopy using quantum cascade lasers (QCL) for in situ diagnostic of plasma processes in industrial environments are reviewed. Examples which emphasize the capability of quantum cascade laser absorption spectroscopy (QCLAS) as plasma diagnostic technique in industrial environments will be given.

Nowadays molecular plasmas play a key role in branches of industry like semiconductor industry, automotive industry, mechanical engineering, light sources, and biomedical technology to name a few. Typical applications are thin film deposition, etching and structuring of semiconductor devices, surface treatment, like activation, passivation and cleaning, and materials and waste treatment as well. The intense use of plasma technological processes demands proper plasma diagnostic techniques for monitoring, controlling and optimization purposes in industrial environments. In particular due to the efficiency of the production process, in situ diagnostic techniques with online capabilities are favorable.

Mid infrared absorption spectroscopy between 3 and 20 µm using QCL has progressed considerably as a powerful diagnostic technique for in situ studies of the fundamental physics and chemistry of molecular plasmas [1]. QCLAS provides a means of determining the absolute concentrations of the ground states of stable and transient molecular species, which is of particular importance for the investigation of reaction kinetics. Since QCL emit near room temperature, i.e. without the need of cryogenic cooling, very compact and robust spectroscopic instruments can be designed. This has stimulated the adaptation of infrared spectroscopic techniques to industrial requirements [2-8].

The aim of the present contribution is to review recent achievements using QCLAS for plasma diagnostics and to emphasize the potential of QCLAS for plasma technological applications in industry.

References

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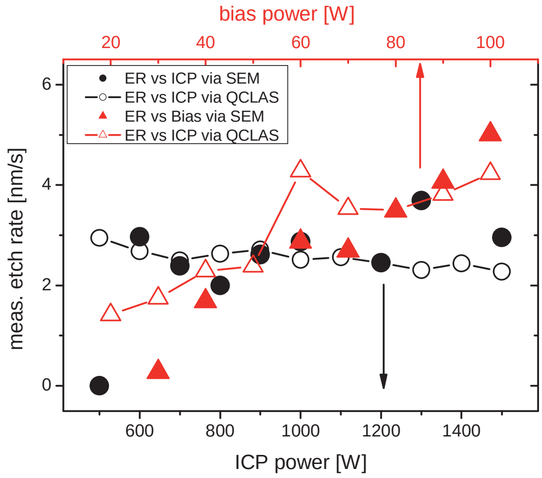

Fig. 1*: Example of in situ measured mean building rate of SiF$_4$ via QCLAS and comparison to ex situ determined etch rates for ultra low-k material (SiCOH) etched in a CF$_4$ plasma.[8]*

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Acknowledgement

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Studies of carbon monoxide emission using Mid-IR QCLAS in methane flames stabilized by nanosecond pulsed discharges

G.D. Stancu[1,2], D.A. Lacoste[1,2], C.O. Laux[1,2]

[1] *CNRS, UPR 288, Laboratoire EM2C, Grande Voie des Vignes, 92290 Châtenay-Malabry, France*
[2] *Ecole Centrale Paris, Grande Voie des Vignes, 92290 Châtenay-Malabry, France, E-mail:* gabi-daniel.stancu@ecp.fr

Atmospheric pressure Nanosecond Repetitively Pulsed (NRP) discharges are used for the stabilization of lean flames, which are less polluting. The understanding of plasma-flame stabilization mechanisms is a current challenge for the scientific community. Here, Mid-IR Quantum Cascade Laser Absorption Spectroscopy (QCLAS) at 2055.4 cm^{-1} was used to measure carbon monoxide densities emitted by plasma assisted methane-air flames. We discuss the challenges associated with the diagnostic techniques and we present measurements of carbon monoxide emissions with and without NRP.

Lean combustion is known to produce fewer pollutants, in particular lower NOx emissions. The drawback of lean combustions is the occurrence of flame instabilities that can lead to flame extinction, hence to unburned hydrocarbons (loss of energy) and the release of pollutants. Nanosecond repetitively pulsed (NRP) discharges have been successfully applied for lean flame ignition and stabilization [1,2]. The use of NRP discharges is a very promising approach, the discharge power being less than one percent of the flame power. Here, lean CH_4-air premixed flames were stabilized by the NRP discharges generated by 10-ns high-voltage pulses (5-10 kV) at pulse repetition frequencies of 30 kHz.

Carbon monoxide is one major combustion intermediate species. Its presence in the exhaust gases is an indication of combustion incompleteness. The first investigations on CO densities in post-flame with and without NRP discharge were performed using Mid-IR QCLAS (QMACS). The presence of high water density (main combustion product) at high temperature (500 – 2000 K) makes the CO detection by Mid-IR absorption techniques very challenging. Through spectral simulations, we have found that interferences of CO lines with water vapor lines are minimal for the CO rovibrational transition P_{21} of the fundamental band at 2055.4003 cm^{-1}. Another difficulty is definition of absorption length for open space experiments. In addition (absorption being a line-of-sight integration technique), analysis must take into account the presence of large temperature and density gradients over the laser beam path. To overcome these difficulties we applied an Abel inversion to the lateral absorbance measurements to obtain local absorption coefficients. Furthermore, we use the measured radial temperature profile to obtain the line strength radial profile, and finally this was used to convert the absorption coefficients into absolute densities. A typical radial CO density is shown in figure 1.

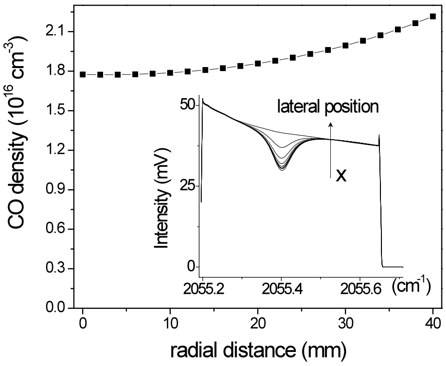

Fig. 1: *CO-density function of radial distance. The inset represents absorption lines at various lateral locations.*

A first set of experiments was performed in the burned-gas region, with the flame confined in a metallic tube of 50-cm length and 8-cm diameter. Single and multi-pass absorption systems were used. The amount of CO decreases by about three orders of magnitude in lean flames compared with rich flames. Using NRP discharges in lean conditions, no significant changes of CO density were observed, whereas in rich conditions an increase of about 20-30 % of the CO density was measured. The second set of experiments was performed for the same plasma and flame conditions without the confinement tube. Using NRP discharges the largest change was obtained for the lean condition at equivalence ratio of 0.7. A factor three increase of the CO density and gas temperature was measured. This demonstrates that the use of NRP discharges at the lean flammability limit enhances substantially the combustion degree.

References

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Infrared gas phase studies in high-current dielectric barrier discharges containing organo-silicon precursors

S. Welzel[1], S.A. Starostin[2], H. de Vries[2], M.C.M. van de Sanden[1,3], R. Engeln[1]

[1] *Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands E-mail: s.welzel@tue.nl*
[2] *FUJIFILM Manufacturing Europe B.V., P.O. Box 90156, 5000 LJ Tilburg, The Netherlands*
[3] *Dutch Inst. for Fundam. Energy Research (DIFFER), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands*

The gas phase of dielectric barrier discharges in roll-to-roll configuration for synthesising SiO_2-like barrier layers from HMDSO or TEOS were studied by infrared absorption spectroscopy. Main products were identified along with their dependence on the (average) power density in pulsed plasmas. Links to earlier model assumptions on the film formation and precursor consumption are provided.

1. Introduction

Silica-like layers formed during large-area plasma-enhanced (PE) roll-to-roll processing of polymeric substrates in diffusive dielectric barrier discharges (DBDs) have been shown to yield high-quality barrier layers [1]. This has been obtained through chemical vapour deposition (CVD) at atmospheric pressure (AP) using organo-silicon precursors and air-like gas mixtures. Provided an electronic stabilisation circuit is applied, high currents in a diffusive discharge mode can be achieved. Complementary gas-phase studies using infrared (IR) absorption spectroscopy were carried out to (i) identify main (dissociation) products in discharges, (ii) study their dependence on the (average) power density in pulsed DBDs, and (iii) to establish links to earlier model assumptions consumption [2].

2. Experimental

The AP PE-CVD setup used was an industrial roll-to-roll configuration (0.5 mm gap). The measurements using a Fourier-Transform IR (FT-IR) spectrometer were therefore carried out *ex-situ*. A small fraction of the effluent of the discharge was sampled under flowing conditions into a multi-pass cell (7 m absorption path) at reduced pressure (~ 50 mbar) to increase the selectivity for different absorption features. The discharge was operated at 185 kHz in a pulsed mode with duty cycles between 10 - 75 %, i.e. plasma-on periods of 0.16 to 1.20 ms. In this way, the precursor dissociation could be studied, even through sampling at the end of the active plasma zone, as at low power densities precursor fragments might be still present.

3. Results

At high (average) power densities the gas phase composition in TEOS or HMDSO containing plasmas is comparable to situations where no precursor is present (fig. 1, [3]) which agrees well with earlier model assumptions about the precursor dissociation along the active plasma zone [2]. Main (stable) species are NO, NO_2, N_2O and HONO as well as carbon containing species such as CO, CO_2 (fig. 1).

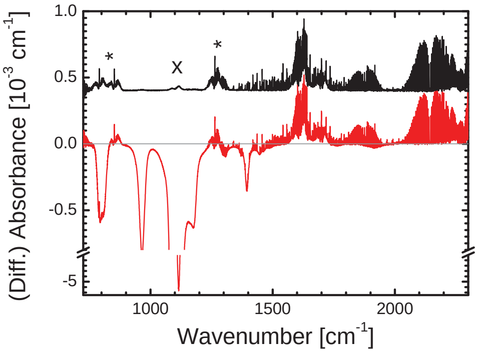

Fig. 1: *FT-IR spectrum recorded in $N_2/O_2/Ar$+TEOS (15/1.8/1.0 slm+ 5 g/hr). The lower trace shows a spectrum (plasma on-off) with an almost complete precursor dissociation (50 % duty cycle). The upper trace (stacked for clarity) highlights the formation of intermediate species: HONO (*), HCOOH (+), precursor traces (x).*

Distinct differences in the product distribution between the two precursors can be seen, particularly at low power densities. Similar to etching conditions (i.e. no precursors present [3]), HCOOH transpires to be a good marker molecule to distinguish different discharge and film formation regimes. Quantitative aspects of selected gas phase species will be discussed along with the analysis of the injected energy.

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SESSION 2

Monday 14th, 16h00

Optically modulated Quantum Cascade Laser – progress towards a frequency comb in the MIR

R. Martini[1], Tao Yang[1], Seong-Wok Park[1], Chao Tian[1], Gang Chen[1]

[1]*Dept. Of Physics and Engineering Physics, Stevens Institute Of Technology,*
1 Castle Point on Hudson, Hoboken, New Jersey 07030, USA
E-mail: rmartini@stevens.edu

We demonstrate the use of optical non-resonant illumination of the front facet of quantum cascade lasers for fast wavelength modulation with the potential of pure frequency modulation. In addition a frequency comb can be generated by optical modulation with Ti:Sapphire laser pulses.

1. Introduction

Middle infrared (MIR) Quantum Cascade Lasers (QCL) [1] have a great potential for spectroscopy due to their high output power, narrow linewidth, and high frequency tuneability. Yet control of the emission wavelength is restricted mainly to a slow temperature or external laser cavity tuning – assisted by indirect wavelength tuning through the heating of the laser based on the current flow.

Yet as most standard spectroscopy techniques have been successfully employed using QCLs, a few promising techniques require more direct control of the lasing mechanism. One example is the utilization of frequency comb generation, which has been extremely successful in optical meteorology and clocks and has recently become a promising spectroscopy technique as well [2] – but requires stable and controlled mode-lock operation of the laser. Here we suggest a novel different approach through optical modulation of the QCL front facet.

2. Optical Modulation

Optical modulation of QCLs has already been demonstrated to allow direct and high-speed modulation of the emission intensity [3] as well as the emission frequency [4]. The inset of figure 1 shows exemplary the frequency response of an 8µm QCL under optical illumination with 100fs short pulses – whereby the detection bandwidth was limited to 8GHz due to the detector. As the signal shows a broadband response with frequencies beyond 10 GHz, a more detailed analysis reveals a discrete emission spectrum consisting of more than 110 harmonics of the 87MHz repetition frequency originating from the modulating Ti:Sapphire laser pulses – as exemplary demonstrated by the 10.35 GHz component shown in the main part of figure 1. This observation proofs the generation of the frequency comb already, and we will discuss and present application of this comb to spectroscopy.

3. Further application

In addition we will present recent developments, which show that same approach can be applied to NIR laser technology as well, allowing generating optical as well as electric modulation of fiber coupled diode laser operating in the 800nm and 1550 nm region. Pure frequency modulation without amplitude modulation can thereby achieved through combination with electrical modulation, which has application in spectroscopy as well as in communication technology.

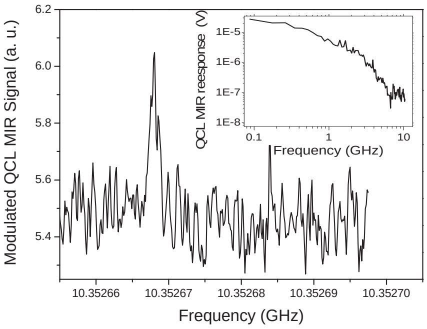

Fig. 1: Inset: Frequency response for optical modulation of QCL, Main: 10GHz component of the modulation response.

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X-ray Spectroscopy of the Megaamper Z-pinches

Zaitsev V.I.[1], Volkov G.S[1]., Grabovskii E.V.[1], Gritsouk A.N.[1], Oleinik G.M.[1], Fedulov M.V.[1],
Bolchovitinov E.A.[2], Rupasov A.A.[2], Shikanov A.S.[2], Novikov V.G.[3], Vichev I.Yu.[3]

[1]State Research Center of Russian Federation Troitsk Institute for Innovation & Fusion Research, Troitsk, Moscow reg.
[2]P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Moscow
[3]Keldysh Institute of Applied Mathematics of the Russian Academy of Sciences, Moscow

Influence of the plasma material on radiation spectra of the high current Z-pinch is investigated. Two different diagnostics (transmitting grid and reflection crystal) for spectroscopy in to the whole of spectral diapason E_{hv} = (50 – 5000 eV) are used. Experimental and calculation results are compared.

1. Introduction

The investigation results of the plasma radiation in Z-pinches at Angara-5-1 facility (currents up to 5 MA) are presented. Multiwires cylindrical W and Al arrays with diameter 12 – 20 mm and the wires diameter 5 –20 µm are used as starting base of the pinch. The column of the dense high temperature plasma with diameter ~1 mm is formed at the final stage of the pinch compression. This plasma radiates soft X-ray (E_{hv} = 50 – 5000 eV) with total issue up to 50 kJ during 5 – 10 ns. To use this X-ray source for different applications it is necessary to know and to control the spectral characteristics.

2. Methods

There are two X-ray spectroscopy diagnostics used for this goal. Diagnostics on the base transmitting diffraction grid is used for analysis of the pinch radiation into very soft spectral region ($E_{hv} \leq$ 1000 eV). Parameters of the grid are the following: material – Au, thickness – 0.6 µm, grid period – 1.4 µm, number of lines is 50. The special film is used as detector of X-ray spectra. To protect the grid from hard electrodes products valve is applied with the time closing ~ 500 µs. Spectrograph with convex mica crystal (2d = 19.9 A) measure the radiation spectra by energy quanta more than 1000 eV. The linear CCD (2048 cells with dimensions 15×15 µm^2) is used for the detection spectral distribution in this device. CCD interface and software provides online processing and presentation spectral picture.

The theoretical model of nonequilibrium radiating multicharge ion plasma, which takes into account the radiation transport and level kinetics of electrons, is used for analysis the experimental data.

3. Results

It was shown that with optimal parameters of the liner (weight, diameter) for current generator the radiation spectrum is determined by atomic weight of wires.

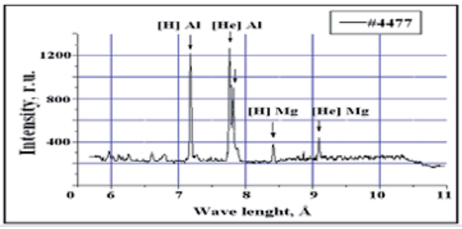

Fig.1. Spectrum of the aluminum pinch.

The pinch radiation of aluminum liners has typical line spectrum (see Fig.1.) which is in agreement with calculations. The [H] and [He]-like lines of aluminum ions are the most intensive. Also one can see K-lines of magnesium that is presented in the using wires (several per cents). The analysis by means comparison of these line intensities gives the following plasma parameters: T_e ~ 550 эВ, $n_e \sim 3 \cdot 10^{20}$ см$^{-3}$ [1]. The increase in the atomic number of substance gives a very high reduction in the intensity of spectral lines. For example, the including small quantity of tungsten wires (about 10%) in to aluminum liner gives decreasing the spectrum line intensity more than one order. The subsequent increasing of tungsten wires transforms the line spectrum into quasi-continuous.

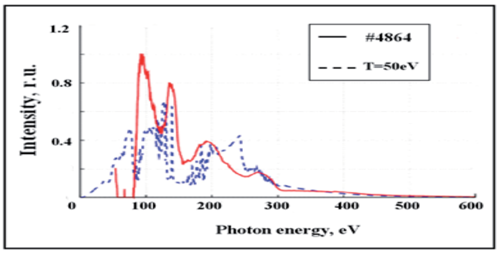

Fig.2. Experimental and calculated spectra of the tungsten pinch.

The large-scale computations were carried out for parameters close to those of the experiment. The atlas spectra form for wide W-plasma parameters (T_e, n_e) was made. The comparison shows that the closest modeled spectra to the experimental data (fig.2) correspond to the following parameters of tungsten plasma: T_e ~ 60 eV, n_e ~ 10^{21} cm^{-3}[2]. Some differences in the shape of the spectra can be explained by the simplifying details of the model.

These researches are supported by the RFBR grant 11-02-01027-a.

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Light Emission from Rare Gases using Combined Electron-Beam and Radio-Frequency Excitation

T. Dandl[1], T. Heindl[1], J. Wieser[2], A. Ulrich[1]

[1]*Physics Department E12, Technical University of Munich, 85748 Garching, Germany*
[2]*Optimare Analytik GmbH & Co KG, Emsstr. 20, 26382 Wilhelmshaven, Germany*

Light emission from rare gases, argon in particular, has been studied using both electron-beam and radio frequency (rf) excitation. Characteristic features of the emission spectra have been measured for a broad wavelength range from ~50 nm to 1000 nm. Strong variations of the intensities of these features have been observed with varying rf-power applied to an electron beam induced plasma. The effects are tentatively attributed to an independent variation of electron density and electron temperature with electron beam and rf power, respectively.

1. Background

A low energy electron beam with a particle energy of about 12keV is sent into gas targets. The technique has been used to build vacuum ultraviolet (VUV) light sources [1] in which rare gases and their mixtures are used as the light emitting media. In order to enhance the intensity and to modify the spectral shape of the light emission, radio frequency power was coupled into the target gas in addition to the electron beam. Besides useful effects for the light sources [2] this combination of two different excitation methods opens an interesting way to study low temperature plasmas, because it allows for the first time to realize "electron beam sustained discharges" (and vice versa “rf-enhanced electron-beam induced plasmas”) in a table top setup.

2. Results

The observed emission spectra show the characteristic features of excited rare gases. The VUV range is dominated by the continuum radiation originating from optical transitions from excited rare gas molecules (excimers) to the repulsive ground state. Excited and ionized rare gas atoms and molecules lead to a further continuum radiation in the deep UV (“third continuum”). Atomic and ionic line radiation appears in the visible and near infrared.

All these structures appear both in sole electron-beam and combined electron-beam rf-excitation, but in modified ways. Increasing the electron-beam current only leads to a rising intensity of the continua as well as the line radiation, proportional to beam current. This is mainly attributed to a higher electron density. Applying additional rf-power increases both the electron and gas temperature. This leads to an enhanced population of higher lying vibrational levels of the excimer molecules, which in turn leads to a strong shift in intensity in the VUV [2]. The so called second excimer continuum originating from vibrationally relaxed molecules is decreased and the so called first excimer continuum increased in intensity. The latter originates from high lying vibrational levels and is emitted on the short wavelength side of the second continuum. As the electron density is assumed to be rather constant for a fixed electron-beam current, the production rate of excimer molecules and therefore the integrated intensity of both continua does not change much.

Rising electron temperature with rising rf-power causes the intensity of atomic lines to increase. This is interpreted by collisional excitation of atoms in excited (metastable) levels.

The continuum emission in the deep UV range, the so-called 3rd excimer continuum, extends from about 170 nm to 250 nm in argon and has been assigned to a combination of optical transitions of various molecular species [3]. With rising rf-power the parts of this structure, belonging to singly ionized molecules, disappear, whereas the parts, belonging to doubly ionized molecules, are enhanced. This effect may also be explained by a higher electron temperature reducing the recombination rate.

Finally, a new feature appears in the emission spectra in the form of a broad continuum extending from the UV to the IR range. As its spectral shape is very similar for all rare gases and its intensity is rising with electron temperature, we assign this emission to Bremsstrahlung.

Funded by the Federal Ministry of Education and Research (13N9528 und 13N11376).

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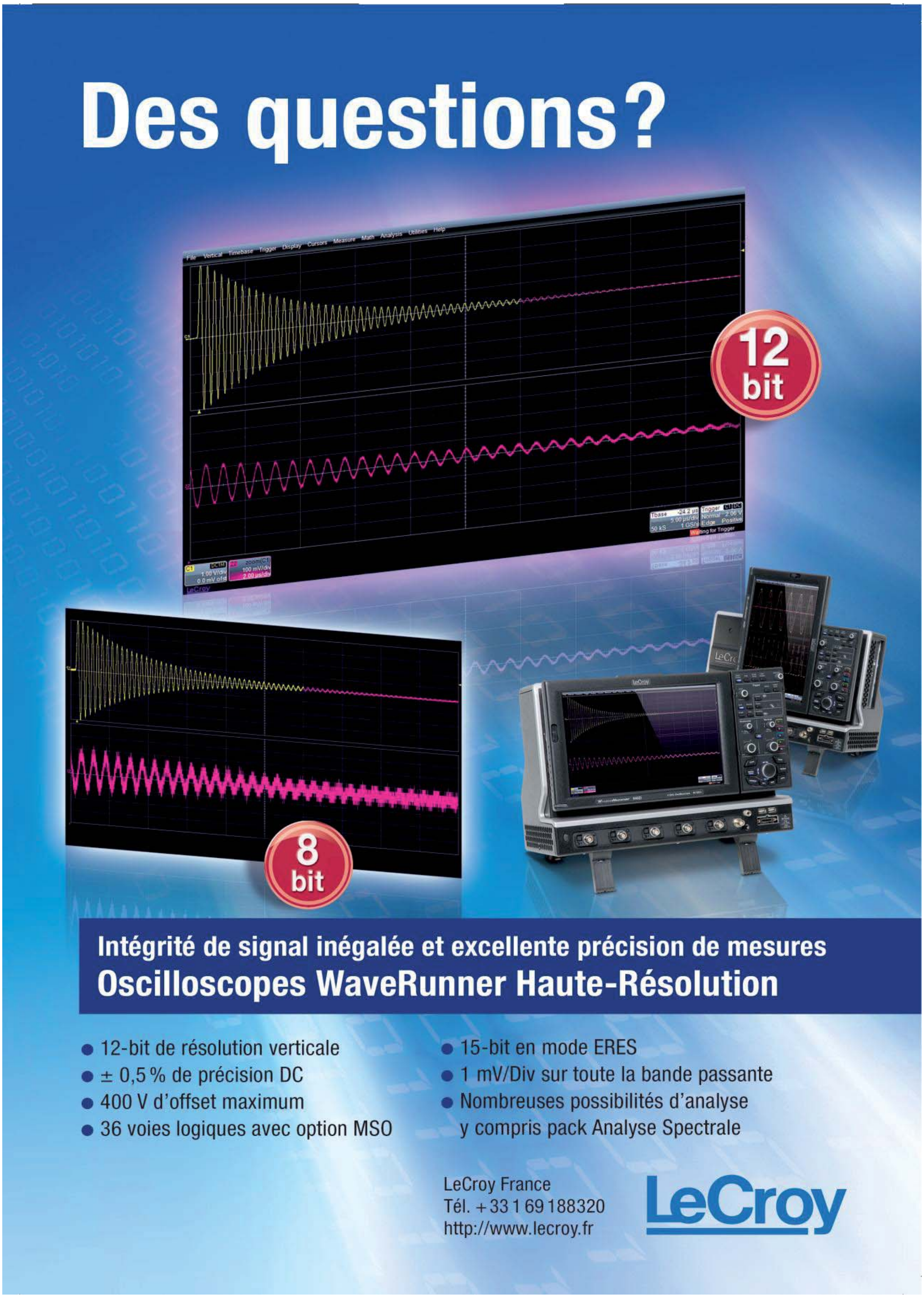
POSTER SESSION &
INDUSTRIAL EXHIBITION

Monday 14th, 17h30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Measurement of the flux ratio of hydrogen atom to film precursor for microcrystalline silicon solar cell

Y. Abe, M. Hori, A. Fukushima, L. Ya, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine

Nagoya university, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan E-mail: y_abe@nuee.nagoya-u.ac.jp

The flux of H atom in plasma enhanced chemical vapor deposition of microcrystalline silicon was evaluated from the measurement of the absolute density and the translational temperature of H atoms. From the measurement, it has been found that the best μc-Si:H can be achieved at the flux ratio of H atom to film precursor of around 80.

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) thin film fabricated by plasma enhanced chemical vapor deposition is promising material for thin film solar cells.

The process margin to get a high quality μc-Si:H thin film for solar cells is very narrow and it is near the transition to a-Si:H growth regime [1]. The transition from μc-Si:H to a-Si:H growth has been recognized to be determined by terms of the H atom flux to silicon deposition flux ratio (Γ_H/Γ_{Si}). The Flux ratios have been reported to be 40 by employing an etch product detection technique and 100 by employing decomposition process of SiH_4 molecules [1,2]. In our work, the flux of H atom is determined from measurement of the absolute density and the translational temperature by vacuum ultraviolet laser absorption spectroscopy (VUVLAS).

2. Experimental and result

Figure 1 shows the schematic diagram of the experimental setup of capasitively-coupled plasma (CCP) with VUVLAS system. A VHF (60 MHz) power of 400 W was supplied to the shower head upper electrode to sustain plasma discharge. SiH_4 gas flow rate was varied from 7 to 15 sccm and H_2 gas flow rate was fixed at 470 sccm. The mixture gases were introduced from the showerhead in the cathode plate. The total pressure was maintained at 1200 Pa (9 Torr). Glass substrates were placed on the grounded electrode. Substrate heating temperature was 523 K. The gap between the cathode plate and substrate was fixed at 10 mm. A crystallinity factor and a preferential orientation were analyzed by Raman spectroscopy and X-ray diffraction (XRD). The VUV laser of wavelength of around 121.6 nm was generated by employing the two-photon-resonance four-wave-sum frequency mixing technique. Slits was used as an end cap of ceramic pipes which adjust absorption length to be 100 mm. To prevent silicon deposition on MgF_2 lenses after gas cell and in front of VUV Monochromator, H_2 gas was introduced in pipes at the flow rate of 30 sccm. The total flow rate of H_2 gas was 500 sccm.

Figure 2 shows the crystallinity factor and the integrated intensity ratio I_{220}/I_{111} in XRD spectra as a function of Γ_H/Γ_{Si}. μc-Si:H of high efficiency solar cell shows (110) preferential orientation and crystallinity factor of approximately 0.6 [3]. Therefore it has been found that the best μc-Si:H can be achieved at Γ_H/Γ_{Si} of around 80.

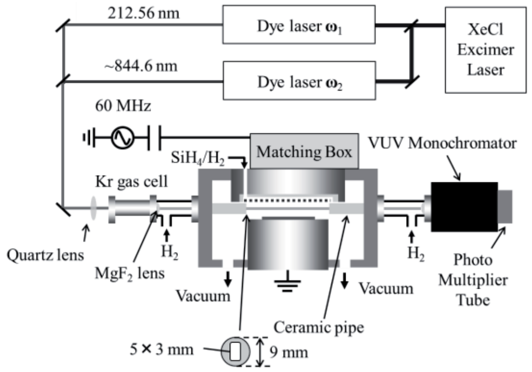

Fig. 1: *Capacitively coupled plasma with VUVLAS system.*

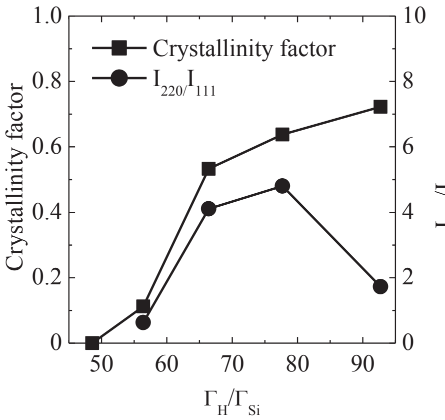

Fig. 2: *Crystallinity factor and I_{220}/I_{111} as a function of Γ_H/Γ_{Si}.*

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Adsorbed phase and gas phase study of isopropanol oxidation by ozone on TiO_2 for surface regeneration

C. Barakat[1], P. Gravejat[2], O. Guaitella[1], A. Rousseau[1]

[1]*Laboratoire de Physique des Plasmas, Ecole Polytechnique CNRS UMR 7648, Palaiseau, France*
[2]*Departement Chimie et Environnement, Ecole des Mines, Douai, France*
(*)christelle.barakat@lpp.polytechnique.fr

A post plasma configuration is used to study the regeneration of the TiO_2 surface -ozone being the main oxidative species- hence limiting the ozonation effect from the real synergic effect between non thermal plasma (NTP) and catalysis in a packed bed reactor model. More importantly, the contributions of the gas phase and of the adsorbed phase for the adsorption and oxidation of isopropanol on TiO_2 are independently monitored using two parallel infrared systems. The complementary analysis of the gas phase composition by FT-IR and the in situ surface analysis of the adsorbent/catalyst by DRIFTS are used to propose an oxidation mechanism for a model COV, isopropanol. This double analytical approach is unique in providing information on the one hand (FT-IR), about the performance of the process in terms of adsorption capacity of materials, oxidation efficiency and surface regeneration and on the other hand (DRIFTS), reaction kinetics in terms of reaction constants, mechanisms of adsorption and oxidation, surface coverage and intermediates formed.

1. Introduction

The peculiarity of the system in place lies in the fact that the plasma is not continuously generated. The pollutant is initially concentrated on the surface of the catalyst and a temporary discharge is then generated to regenerate the surface by mineralization of the adsorbed organic species.

In the gas phase apparatus, the system consists of a dielectric barrier discharge (DBD) reactor, a catalytic reactor and the FT-IR cell in series, enabling the analysis of the gas phase composition at the output of the catalytic reactor. In the solid phase apparatus, the adsorbent bed is located inside the DRIFTS cell, also placed downstream from the plasma reactor, and the contact between the gas and the solid is monitored in situ, allowing a real time analysis of the phenomenon taking place on the surface.

2. Gas phase and surface studies of IPA

2.1. Adsorption of IPA on TIO_2

IPA, commonly found in confined air is tested on TiO_2, also known for its photocatalysis potential [1,2]. The gas phase study shows an adsorption capacity of 240µmol per gram of TiO_2. The DRIFTS experiments are performed in similar conditions and using the same experimental steps, these have shown that IPA adsorbs on the surface via two different mechanisms, a dissociative process and a non dissociative process. The dissociative adsorption results in the formation of monodentate isopropoxy groups and surface hydroxyl species and the non dissociative adsorption giving rise to strongly bonded isopropanol and weakly hydrogen bonded isopropanol [3,4,5].

2.2 Oxidation of IPA on TiO_2

The plasma was able to oxidize 2% of the adsorbed IPA, a transient production of acetone is also observed in the gas phase when the plasma is switched on. The adsorbed phase study of the ozonation step shows that acetone is the main intermediate in the oxidation route of isopropanol into CO_2 and CO (figure 1). Surface kinetics are studied and show that the rate constant for IPA consumption on TiO_2 via plasma enhanced catalysis is $1.34 \times 10^{-3} s^{-1}$, twice more efficient than photocatalysis alone [5].

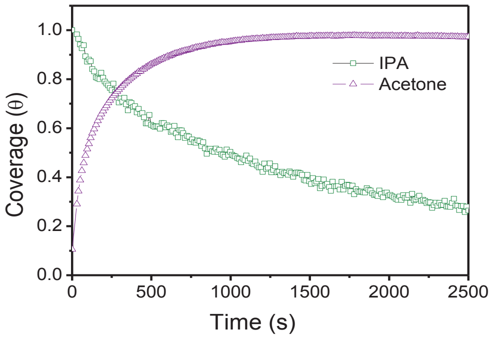

Fig. 1: *Evolution of surface species on TiO_2 during the ozonation of IPA*

3. Conclusion

For further elucidation, a study of the adsorption and reactivity of acetone during plasma is performed and analysed by the complementary analytical methods, FT-IR and DRIFTS. A mechanism is then proposed for the oxidation of IPA on TiO_2 whereby two types of sites, denoted s_1 and s_2, are distinguished and only one leads to the complete oxidation of IPA.

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Time-resolved LIF measurements in a low pressure magnetized DC discharge

G. Bourgeois[1], A.Lejeune[1], N. Sadeghi[2] and S. Mazouffre[1]

[1]*ICARE-CNRS, Orléans, France*
[2]*Univ. Grenoble 1 / CNRS, LIPhy UMR 5588, Grenoble, F-38041, France,*

Oscillations in space and time of Xe^+ metastable state velocity distribution function are measured by means of time resolved laser induced fluorescence spectroscopy in the magnetized discharge of a Hall effect thruster. A photon-counting technique is used to detect the weak fluorescence signal.

Evolution in time of the velocity distribution function (VDF) of xenon ion is measured in the cross-field DC xenon discharge of a Hall effect thruster. Xe^+ metastable 5d $^2F_{7/2}$ state is probed by means of laser induced fluorescence (LIF) spectroscopy at reference wavelength of 834.7233 nm. Fluorescence light is detected at 541.9 nm. Time resolution of 1 µs is required as oscillation frequency ranges around 15 kHz in our device. Classic LIF spectroscopy uses phase sensitive detection with laser beam intensity modulation. This method, efficient enough to extract a low signal in a high background noise, cannot achieve the time resolution required. Thus a time-resolved photon counting system was built [1] in order to capture a fluorescence signal as weak as a single photon with a time resolution of 100 ns.

Oscillation of the complete Xe^+ VDF is reconstructed thanks to the measurement of the oscillation of several Xe^+ velocity groups with a width ~ 60 m/s. As photon flux is low, around 5 per 100 ns, signal accumulation is necessary to build up the oscillation of an ion velocity group. This is easily done when the oscillations of the discharge are stationary, in other words when the phase of the oscillations is constant or spectral power distribution sharply distributed around one frequency. In this case, one needs to synchronize the acquisition set up with this frequency. As oscillations are strongly non stationary in our device, other solutions were found.

The first solution [2] was to define a phase to the plasma oscillations using a fast-interruption of the power supply. This brings a strong re-ignition of the plasma which disturbs the normal operating regime. By synchronization of the acquisition system with this periodical shutdown, accumulation of photons was possible. Fig.1 displays a 2D map of the time evolution of Xe^+ VDF at one position in space. It was built by interpolating the raw time evolution of 12 Xe^+ velocity groups. This technique needs almost no data analysis but requires long time acquisition, around 5 hours for Fig.1, and it disturbs the natural discharge behaviour.

Another method was investigated to get rid of the interruption system. The main idea is the direct acquisition of the oscillating fluorescence signal using the photon-counting system, with large data post-processing using wavelet or empirical mode decomposition analysis [3].

A preliminary case has been studied. Instead of synchronizing the oscillations using a fast-interruption device so as to put them in phase, resonance frequency of the plasma discharge was stimulated. This was achieved by applying a 200 V amplitude modulation on a floating electrode placed close to the cathode [4]. Frequency of this modulation was tuned so as to find a resonance of the system in the 15 kHz range. Average values such as discharge current or time-averaged Xe^+ VDF were unchanged by applying the modulation. This technique allows simple data post-processing using FFT while minimizing the disturbance of the plasma discharge. As preliminary result, one ion group velocity is studied. Acquisition of 10^4 periods of fluorescence signal is performed and data analysis shows its oscillation at the reference frequency. This method is much faster than the one previously described with limited disturbance of the discharge and good results with limited analysis. It seems thus promising for future extensive work on time-resolved LIF spectroscopy in non stationary plasma discharges.

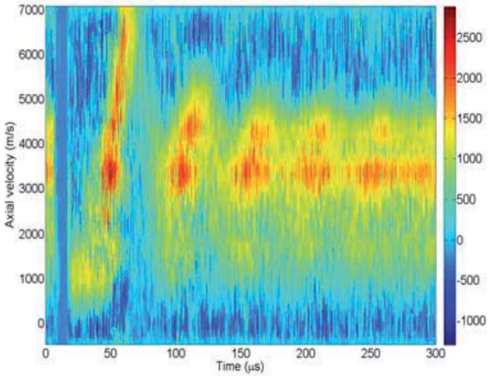

Fig.1 ***Oscillation of Xe^+ VDF***

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OES diagnostics of underwater diaphragm discharge generated by HV pulses at atmospheric pressure

A. Brablec[1], O. Galmiz[1], Z. Navratil[1]

[1]*Dept. of Physical Electronics, Masaryk University, 61137 Brno, CZ, E-mail: abr92@elanor.sci.muni.cz*

Underwater diaphragm discharge generated by HV pulses at atmospheric pressure has been studied by OES to estimate basic parameters such as electron density and temperature of excited species for various experimental conditions.

1. Introduction

Underwater electrical discharge systems attract attention of many research groups mainly for its proven efficiency in the wastewater remediation [1]. Recently emerged application for underwater discharge offering substantial economical and environmental benefits compared with conventional wet chemical methods is the surface functionalization of textile materials [2]. So far, only a small number of works has been published about diagnostics of the discharge itself due to the main concern for material treatment [3, 4] and also due to the complicated nature of filamentary underwater plasma.

2. Experimental setup

The discharge was generated between two metallic electrodes at 2 cm mutual distance. The electrodes were connected to a pulsed HV power supply based on the double rotating spark gap. The propagation of discharge filaments could be influenced by parameters such as voltage, water conductivity, etc. The maximum peak voltage was 30 kV DC. The maximum repetitive rate of pulses was 60 Hz. The water conductivity range was from 0.5 to 3.7 mS/cm. Principal schema of the experimental set-up can be found in [5].

The discharge was studied with optical emission spectroscopy of the light coming from narrow discharge region between the electrodes. The spectra were measured by means of HR640 spectrometer, Jobin - Yvon (grating 1200 grooves, focal length 640 mm, CCD detector cooled by nitrogen). Molecular spectra bands of CN violet system ($B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$, $\Delta v = 0$) were used for determination of vibrational temperature. H_α line profile was used to determine electron temperature and density by the standard Griem's table.

3. Results and discussion

The example of intensity dependences of emissions of CN ($B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$, 0-0) and hydrogen ($H_\alpha$) on discharge voltage is displayed in Fig. 1. The intensity of CN band is decreasing with increasing applied voltage, in contrast with H_α. This can be attributed to the observation, that the filaments became brighter and longer with increasing voltage in the interelectrode region.

The vibrational temperature of CN remains approximately the same with increase of voltage, whereas increasing the water conductivity causes substantial rise of vibrational temperature.

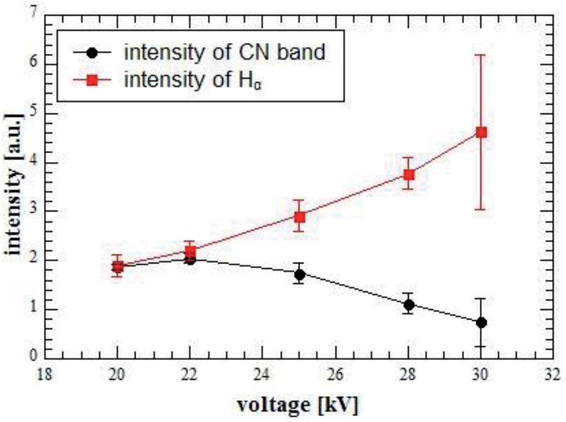

Fig. 1: *Intensity of selected components in OES spectra versus applied voltage for HV power supply based on double rotating spark gap.*

Acknowledgments: This research was supported by the Ministry of Education of the Czech Republic under Project CZ.1.05/2.1.00/03.0086.

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Dissociation study on CO_2 in an atmospheric pressure plasma

F. Brehmer[1], S.Welzel[1], S. Ponduri[1], M.C.M. van de Sanden[1,2], R. Engeln[1]

[1]*Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, E-mail: s.welzel@tue.nl*
[2]*Dutch Inst. for Fundam. Energy Research (DIFFER), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands*

An atmospheric pressure dielectric barrier discharge for the conversion of CO_2 to CO is presented. To optimize the optical access for *in-situ* diagnostics, the setup is designed in a parallel plate configuration. Infrared absorption spectroscopy along with careful electrical characterization are carried out to analyse the gas composition and establish energy efficiencies.

1. Introduction

In any scenario for storing renewable energy in value-added hydrocarbons produced from CO_2, the dissociation into CO is known as the process limiting step. To surpass the limitations observed for conventional (photo-)catalytic production routes, plasma processing is now considered as alternative approach. Non-equilibrium plasmas can be used to selectively excite vibrational levels of CO_2 which is known to result in high dissociation efficiencies [1]. In this way, the highly endothermic dissociation of CO_2 is separated from subsequent hydrogenation steps. We report on an atmospheric pressure plasma process for the dissociation of CO_2 using a dielectric barrier discharge (DBD), which has a large potential for future up scaling [2].

2. Experimental Setup

The symmetric DBD is designed as flow-tube in parallel plate configuration to achieve optimal optical access for *in-situ* diagnostics. Figure 1 shows a sketch of the discharge reactor and a N_2 plasma at 1 bar, which is usually much brighter than CO_2 in the visible range under similar experimental conditions.

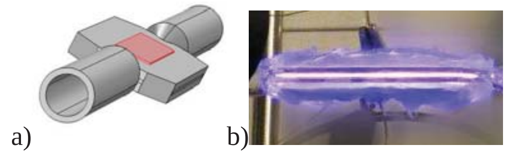

Fig. 1: a) *Sketch of the discharge tube with electrodes attached.* b) *N_2 discharge in the tube.*

The active discharge zone of 1 mm gap width is enclosed by quartz plates serving as barrier. Metal electrodes are mounted on the outside of the dielectric material. This specific design allows direct access to the active plasma zone to carry out optical emission spectroscopy and provides a convenient basis for electronic modifications of the mid-frequency (kHz) matching circuit.

The experiments were performed in pure CO_2 at atmospheric pressure to achieve maximum efficiency in running costs of the final process. Furthermore gas flow rates in the range of 0.1 to 3 slm were investigated to set a link to high throughput situations.

3. Results

A thorough electrical characterisation was essential to specify the energy efficiency: The injected power was recorded directly via voltage and current measurements as well as using Lissajous figures.

The dissociation of CO_2 to CO and by-products was studied downstream of the flow reactor using Fourier-Transform infrared (FT-IR) absorption spectroscopy. In first experiments, CO and significant amounts of O_3 could be measured. The produced CO scaled weakly with the injected power (figure 2). The analysis of both absorption features, ν_1 and $2\nu_1$, yield the same trend. However, the fundamental CO band (ν_1) was close to saturation while the lines of the overtone band of CO ($2\nu_1$) were of low signal-to-noise ratio.

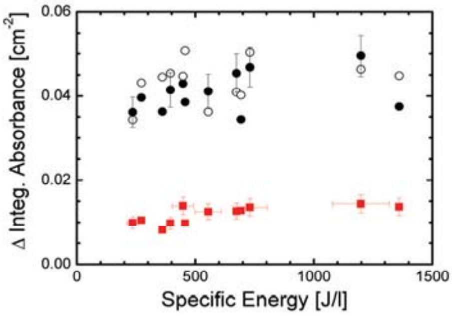

Fig. 2: *Species measured downstream of the flow reactor with FT-IR: full circle = CO ν_1, open circle = CO $2\nu_1$ (x10), squares = O_3.*

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Atomic Emission Spectroscopy – the tool of optimization of the aluminium nitride thin films synthesis by reactive magnetron sputtering method for electronics applications

R. Chodun[1], K. Nowakowska-Langier[2], K. Zdunek[1,2]

[1]*Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141 02-507 Warsaw, Poland, E-mail: rchodun@op.pl*
[2]*National Centre for Nuclear Research (NCBJ) , Andrzeja Soltana 7, 05-400 Otwock-Swierk, Poland*

This paper reports the results how to optimize the process of synthesis of aluminum nitride thin films basing on the analysis of plasma emission spectra excited by magnetron sputtering of aluminum in the reactive nitrogen atmosphere. The dual magnetron sources operating in continuous and impulse gas flow was used in the experiment. The UV and VIS plasma emission spectra were measured by use of OES and monochromator devices. Analyses were made by comparing the positions and intensities of spectral lines of plasma individual components. The obtained spectra was related to the chemical characteristics of synthesized films and their utilitarian properties. Our work has shown that the use of plasma atomic emission spectrometry at the stage of the synthesis process allows to control its course, and thus plays a very significant role in its diagnostics.

1. Abstract

Nowadays the growing interest in the abillity of AlN films synthesis by magnetron sputtering method for applications in modern electronic devices is noticable. Hitherto, most common methods used for synthesis of AlN layers were CVD or MOCVD methods, which the most significant feature is high temperature of process. The use of plasma assisted methods from the PVD group like the pulsed magnetron sputtering method is a very interesting and promising alternative not only because of the possibility of an efficient synthesis of AlN films at lower temperatures, but also because of the chemical purity, which fact is problematic in the case of CVD methods. The issue of aluminium nitride films for electronics synthesized by magnetron sputtering recently has become a subject of interest to laboratories in the world not only due to the properties of nitride, but also because of the positive features of the method of synthesis. The results described in the literature seem to be encouraging, but emphasize the issues typical for the initial stage of development (structural and chemical properties of AlN layers selected in the context of a specific application).

W have supposed that AES (Atomic Emission Spectroscopy) would make the opportunity to full control the process of synthesis and indirectly, characterized synthesized films. The dual magnetron system (Gemini) operating in AC mode and DC magnetron were used in the experiment. Processes of synthesis were carried out in the atmosphere of a mixture of argon (as the source of ions sputtered the material of cathode) and nitrogen. The UV and VIS plasma emission spectra were measured by use of OES and monochromator devices. Analyses were made by comparing the positions and intensities of spectral lines of plasma individual components. Gathered information allowed us to characterize the synthesis under the various conditions of pressure and power distribution more precisely what is reported in this work. The measured spectra was related to the chemical characteristics of synthesized films (investigated by Raman spectroscopy technique) and their dielectric properties.

Our work has shown that the use of plasma atomic emission spectrometry at the stage of the synthesis process allows to control its course, and thus plays a very significant role in its diagnostics.

Comparison of methods of self-absorption and effective branching fractions for metastable densities determination in surface-wave neon plasma

L. Dosoudilová[1], Z. Navrátil[1], T. Bogdanov[1,2], E. Benova[2], J. Hnilica[1], V. Kudrle[1],
A. Brablec[1]

[1] *Masaryk University, Kotlarska 2, 61137 Brno, Czech Rep., E-mail:ldosoudi@mail.muni.cz*
[2] *Sofia University, 27 Kosta Loulchev Str., 1111 Sofia, Bulgaria*

Surface-wave sustained microwave discharge in neon at low pressure was studied by optical emission spectroscopy to determine the metastable state densities of $1s_3$ and $1s_5$ levels for different pressures. The method of branching fractions was investigated and compared with self-absorption method.

1. Introduction

Coaxial microwave discharge sustained by travelling electromagnetic wave is a new type of plasma source proposed for example in [1]. In our experimental set-up the chamber consists of two coaxial quartz tubes and a metal rod, which is arranged at the tubes axis. Plasma properties strongly depend on the geometry factors like tube or metal rod radius, tube wall thickness, as well as on the gas pressure. These dependences have been studied theoretically [2, 3], but not yet confirmed experimentally.

2. Experimental

The MW discharge was generated by a magnetron power generator with maximum power of 100 W, which was fetched via a coaxial cable into a metal rod-shaped antenna, surrounded by air at atmospheric pressure. The total length of the tube was 320 mm. The interspace between the cylindrical walls was filled with neon gas up to pressure of 300 – 700 Pa. The discharge was sustained in the flowing regime with gas flow rate approx. 6.6 – 27.0 sccm.

The emission of radiation from the plasma was studied by OES with Jobin Yvon HR 640 spectrometer. The spectra were measured at the tube end in the axial (or longitudinal) direction, sensing the light from the whole plasma column.

The method of effective branching fractions (EBF) [4] was used to determine neon $1s_3$ and $1s_5$ metastable state densities from transitions $2p^5\,3p \rightarrow 2p^5\,3s$ for different pressures. The determined densities were compared with our previous results obtained from self-absorption method [5].

EBF is based on comparison of photon emission rates of lines coming from the same 2p level (Paschen notation). The branching fractions depend due to the reabsorption of radiation on densities of lower 1s levels and can be calculated from Einstein coefficient for emission and from escape factor according to Mewe approximate expression [6]. Marquardt-Levenberg algorithm for least squares method was used for fitting of the theoretical values of fractions to the measured one to determine metastable densities.

3. Results and discussion

21 transitions from levels $2p_2$, $2p_4 - 2p_8$ were used in the calculations. The determined densities depended on gas pressure ranging $2.5 - 3.7 \times 10^{10}\,\mathrm{cm}^{-3}$ for $1s_5$ state, that corresponds with values from self-absorption method, i.e. $3.2 - 4.2 \times 10^{10}\,\mathrm{cm}^{-3}$.

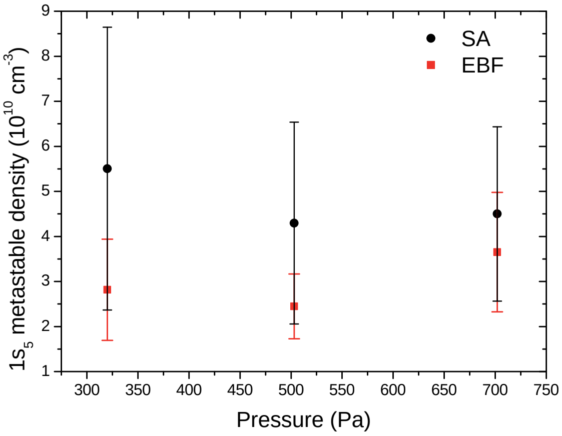

Fig. 1: *Pressure dependencies of density of $1s_5$ state from self-absorption method and branching fraction.*

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QCL-Optical FeedBack Cavity Enhanced Spectrometer for real time monitoring of Formaldehyde: application to air plasma treatment system.

E.Fasci[1], O. Guaitella[1], P. Gorrotxategi Carbajo[2], I.Ventrillard[2], M. Carras[3], Maisons[3], D. Romanini[2], A. Rousseau[1]

[1]*LPP, Ecole Polytechnique, UPMC, Université Paris Sud-11, CNRS, Palaiseau, France*
[2] *Laboratoire Interdisciplinaire de Physique (LIPhy), CNRS UMR 5588, Université J. Fourier de Grenoble, 38402 St Martin d'Hères, France*
[3] *Alcatel Thales III-V lab, Av. Augustin Fresnel, Campus Polytechnique, Palaiseau, France*

A Mid-Infrared Optical Feedback-Cavity Enhanced Absorption Spectroscopy (OF-CEAS) system has been implemented for highly sensitive trace gas detection in order to validate the efficiency of a plasma/catalyst coupling device for formaldehyde destruction in indoor air treatment.

Formaldehyde, the simplest of the aldehydes, is considered to be one of the most toxic compound present in strong concentrations in the inside air. It also represents a good indicator of indoor pollution level since it is an oxidation product of many Volatile Organic Compounds (VOC).

Moreover the International Agency for Research on Cancer (IARC) classified formaldehyde as a carcinogenic substance. Thus the need to monitor indoor spaces has become of public priority.

In this respect we developed a high sensitively spectrometer for real time monitoring of CH_2O based on cavity enhance absorption spectroscopy (CEAS). with optical feedback (OF) [1] and a cascade quantum laser (QCL).

The spectrometer will be applied to the study of depollution processes by means of Non Thermal Plasma [2]. A Dielectric Barrier Discharge reactor will be combined with different adsorbant/catalytic materials such as TiO_2, Al_2O_3, MnO_2. A destruction efficiency will be studied with varying input energy into the plasma at different values of formaldehyde concentration.

The OF-CEAS system is based on a continuous wave Distributed Feed Back Quantum Cascade Laser (DFB-QCL), realized at Thales-III-V lab [3]. This single mode laser emits at a wavelength of 5.65 μm at room temperature. It has been employed to match molecular fundamental vibration transitions of formaldehyde (H_2CO) , which possess in this spectral region significantly stronger absorption features compared to the near infrared.

The laser radiation, which can be tuned over about 7 cm^{-1} by temperature, is directly coupled to a high finesse (HF) V-shaped cavity. The particular shape of the HF cavity allows just the intra-cavity radiation to feed back to the laser and as a result to optically lock the laser frequency in rapid succession to each cavity mode in the range covered by a laser current scan. Spectral data points correspond to cavity modes, which are uniformly spaced and offer a spectral resolution of 150 MHz (0.005 cm^{-1}) for a 1m long V-shape cavity with a spectral definition in the 10 kHz range. In addition the high reflectivity of the mirrors provides an optical interaction path of about 10 km. Working at a cavity pressure of about 50 mbar, with a sample gas flow in the range of tens standard cubic centimeter (sccm), a minimum detectable absorption coefficient of 1×10^{-9} cm^{-1} was demonstrated in 100 ms of integration time (single laser scan) which for CH_2O corresponds to a detection limit of 120 ppt. A preliminary study of the Allan Variance of the measured data shows that averaging over 10 seconds yields an improvement of 10 times, leading to a detection limit down to the 10 ppt range.

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Studies of self-modulation phenomena in high-frequency electrodeless lamps

Z. Gavare[1], A. Svagere[1], J. Skudra[1], V. Fyodorov[1]

[1]*Institute of Atomic Physics and Spectroscopy, University of Latvia, Skunu street 4, Riga, LV-1050, Latvia E-mail: zanda.gavare@gmail.com*

In this work we present studies of self-modulation phenomena in high-frequency low-pressure electrodeless discharge lamps filled with BiI_3+Ar and $SnCl_2$+Ar.

1. Introduction

High-frequency electrodeless discharge lamps (HFEDLs) are well known as bright light sources emitting narrow and intensive spectral lines in broad spectral region (from VUV to IR). HFEDLs have been used in various scientific devices, for example, in absorption spectrometers, and they are well suited for the investigation of plasma interaction with the lamp bulb, due to the absence of electrodes.

The HFEDL vessels are mostly made of SiO_2 glasses and filled with different metal vapors and rare gases at low pressure. High frequency electromagnetic field is applied to induce an inductively coupled discharge. The excitation frequency of the applied high-frequency field is 100 MHz. Initially, the discharge occurs in buffer gas. The increase in temperature leads to the increase of metal vapor pressure, and then the emission of the working element can be observed.

The performance of HFEDLs depends strongly on many preparation conditions, for instance, the type and amount of buffer gas and working element. Depending on amount of working element and operating regime, the self-modulation phenomena can be observed, namely, periodical fluctuations of the emission intensity.

In this work we present studies of self-modulation phenomena in HFEDLs filled with BiI_3+Ar and $SnCl_2$+Ar.

2. Experimental part

The plasma under study was several HFEDLs filled with (1) BiI_3+Ar and (2) $SnCl_2$+Ar. The buffer gas pressure was 3 Torr.

The HFEDLs were operated at different excitation generator voltage values (20-30V), and the emission spectra changes in time were analyzed. The emitted light spectra were registered using AVANTES AVS-PC2000 plug-in spectrometer with a 2048-element linear CCD-array detector. The spectra were recorded in the wavelength range from 190 till 850 nm.

For more detailed studies of self-modulation regime of HFEDLs, the spectrometer JobinYvon SPEX 1000M (grating 1200 $l\cdot mm^{-1}$, focal length 1 m) with charge-coupled device matrix detector (2048 ×512 Thermoelectric Front Illuminated UV Sensitive CCD Detector, Simphony) was used.

It was observed that in some cases one could register presence of different impurities, like OH or CN. Spectra of these molecules can be used to determine plasma temperature. In these measurements, the intensity distribution over the rotational lines of OH ($A^2\Sigma^+ \rightarrow X^2\Pi$; v = v' = 0, Q1-branch at 306.4 nm) was used to determine the plasma temperature. This method is described in details elsewhere [1].

3. Results and conclusions

These measurements showed that self-modulation regime mostly can be observed at higher voltage values of excitation generator. For example, for $SnCl_2$+Ar lamp such regime can be observed only at 29 V and higher, but for BiI_3+Ar HFEDL it can be achieved even at 25 V. This is determined by the amount of the working element filled in the lamp.

The occurrence of such regime can be explained by the increase of plasma temperature with following increase of metal vapor pressure and amount of halogen in plasma, which leads to the quenching of emission. After the cooling period, the discharge is excited again. The frequency of self-modulation is about one minute, and it depends on the filling and operating conditions.

Acknowledgment

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Optical emission spectroscopy for diagnostic and monitoring of O_2 plasma used for modifications of tin sulphide thin films

A. Gómez[1], H. Martínez[2], M. Calixto-Rodríguez[3], D. Avellaneda[4], P.G. Reyes[1]

[1]*Facultad de Ciencias, Universidad Autónoma del Estado de México, Estado de México, México*
[2]*Instituto de Ciencias Fisicas, Universidad Nacional Autónoma de México, Apartado Postal 48-3, 62251, Cuernavaca, Morelos, Mexico*
[3]*Centro de Investigación en Energía, Universidad Autónoma del Estado de México, Estado de México, México*
[4]*Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, México*

Oxygen plasma used for modifications thin films has been study for optical emission spectroscopy (OES). The species observed were O, SnS, S_2, Sn, Sn^{2+}, S and S^+, which they have been formed from dissociative excitation of the O_2 and SnS under electron impact. No correlation has been found between the O emission and the modification of the electrical and optical properties of the tin sulphide thin film. However, as the time of treatment is increased the electrical and optical properties of the thin films decreased.

1. Introduction

The search for new materials and its application on photovoltaic devices is a topic in which many research has taken place nowadays due to the importance for the development of new energy sources for an impact in the environmental care. In the manufacture of solar cells the most important production is in Silicon based cells, this has the difficulty of a high cost production and handling difficult; new research has brought the development of cells based on materials as Tellurium, Cadmium or Selenium, which have the inconvenient of low abundance or toxicity. This makes the tin sulphide a promising material for application in solar cells as absorber layer, being a low cost material, abundant and non-toxic, combined with its optical and electrical characteristics.

This work is based on the plasma treatment of SnS tin sulphide films with an atmosphere of Oxygen with the aim to enhance its optical and electrical properties for raise the sunlight absorption and improve its efficiency.

2. Experiment

The samples treated in the experiment was deposited by chemical bath [1] with thickness of 500 nm.

2.1. Plasma treatment

The post-deposition treatment in oxygen plasma was carried out in the SnS thin films at a pressure of 3 Torr. The experimental arrangement used to generate the plasma was described on detail elsewhere [1].

2.2 Results

The emission spectra of oxygen plasma are shown in Fig. 1. The species observed were O, SnS, S_2, Sn, Sn^{2+}, S and S^+, has been found to result from dissociative excitation of the O_2 and SnS under electron impact.

The samples treated with Oxygen show a change in their coloration (from dark brown to yellow) which indicates a phase change to SnO_2. This make possible generate this compound for application as substrate in solar cells. Also, This Phase is an indication of the correlation between O line and modification of the sample. The band gap value found was 2.1 eV, according to previous reports.

For the resistivity measurements, we have a conductivity of $7.00 \times 10^{-6}\ \Omega^{-1}\text{-cm}^{-1}$ for the samples untreated, while $1.95 \times 10^{-1}\ \Omega^{-1}\text{-cm}^{-1}$ for the samples treated. It shows an increase in the conductivity, which it is attributed to the O line observed in the experiment.

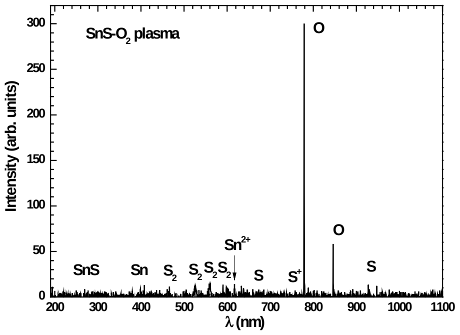

Fig. 1: *OES spectrum for SnS-O_2 plasma.*

Acknowledgments

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On investigations of the reaction kinetics in dust producing rf discharges in gas-mixtures of Argon or Helium and hydrocarbons

F. Hempel[1], D. Lopatik[1], B. Sikimić[2], I. Stefanović[2], J. Winter[2], J. Röpcke[1]

[1]*INP Greifswald, Felix-Hausdorff-Str. 2, 17489 Greifswald, Germany*
2Institute of Experimental Physics II, Ruhr-University Bochum, 44780 Bochum, Germany

MIR tuneable diode laser absorption spectroscopy (TDLAS) and Fourier transform infra-red (FTIR) spectroscopy techniques were applied to investigate chemical phenomena in hydrocarbon containing Ar/He dusty plasmas. From the molecular concentrations the precursor molecules and of the produced hydrocarbons fragmentation respectively conversion rates were calculated. These rates were found to be in a comparable order of magnitude as in surface wave discharges or in planar microwave plasmas.

1. Introduction

The volume chemistry of low temperature molecular plasmas containing hydrocarbon precursors has been of great interest over the past decade. It is well known, that polymerization processes in these discharges may cause the formation of particles with a diameter up to several hundreds of nanometres in the plasma volume. In this contribution we focused on the hydrocarbon chemistry in relation to dust particle formation in Ar and He RF plasmas of a capacitively coupled parallel plate reactor with admixtures of C_2H_2 and CH_4 to improve the understanding of plasma chemical phenomena in this dust forming plasma.

2. Experimental

The temporal evolution of the concentrations of the methyl radical and of four stable molecules, C_2H_2, CH_4, C_2H_4 and CO has been monitored by infrared tunable diode laser absorption spectroscopy (IR-TDLAS) with a compact and transportable multi-component acquisition system (IRMA). The particle growth was monitored by absorbance measurement at 5000 cm^{-1} using an FTIR spectrometer. All measurements were performed in a radio-frequency (rf) capacitively-coupled parallel plate reactor working at f= 13.56 MHz by an applied power of P= 15 W. The pressure was p= 0.1 mbar for typical flow rates of 8 sccm Ar, 0.5 sccm C_2H_2 or 1 sccm CH_4.

3. Results and discussion

Fig. 1 shows an example of time dependence of concentrations of molecular species measured by TDLAS in Ar and He plasmas with admixtures of C_2H_2 or CH_4. It can be seen, that in an Ar-C_2H_2 plasma (phase 1), concentrations of CH_4 and CH_3 were below the detection limit. After about 10 min, the C_2H_2 flow was stopped and CH_4 was added as precursor. With this precursor CH_3 and C_2H_2 were found to be in the range of 10^{11} and 10^{12} molecules cm^{-3}, respectively. It is interesting to note, that the concentrations of all species were strongly correlated with the dynamic of the dust formation (not shown).

The degree of dissociation of C_2H_2 in phase 1 was found to be ca. 95 % while the value for methane in phase 3 and later varied between 45 and 90 %, depending on the presence of dust particles in the chamber and on the Ar or He plasma conditions. It is well known that the presence of the dust particles can significantly change plasma parameters like the mean electron energy. With the disappearance of the dust, the mean electron energy decreases and this causes a reduced degree of dissociation of CH_4, while the density of C_2H_2 is slightly increased.

The measured concentrations were used to calculate absolute fragmentation rates of C_2H_2 and CH_4 and conversion rates to the main products. The fragmentation rates were in the range of 3.2 x 10^{16} J^{-1} (C_2H_2) and of methane at 0.16…2.5 x 10^{16} J^{-1} (CH_4). The conversion rates to the produced hydrocarbons were in the range of 0.23…8.5 x 10^{14} J^{-1}.

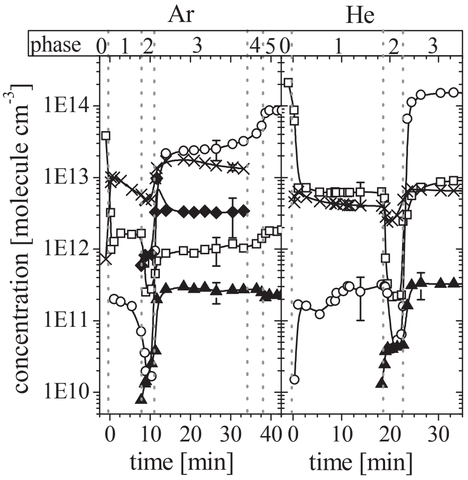

Fig. 1: *Molecular concentrations in Ar (left) and He (right) RF plasmas with admixtures of C_2H_2 or CH_4 as a function of the time (☐ - C_2H_2, ○ - CH_4, ◆ - C_2H_4, ▲ - CH_3, × - CO).*

Spectroscopic measurements in plasma generated by waveguide-supplied coaxial-line-based nozzleless microwave source

B. Hrycak[1], M. Jasiński[1], J. Mizeraczyk[1, 2]

[1] *Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdansk, Poland*
[2] *Department of Marine Electronics, Gdynia Maritime University, Morska 81-87, 81-225 Gdynia, Poland*

In this paper, results of spectroscopic measurements in microwave plasma at high argon flow rates are presented. The plasma at atmospheric pressure was generated in waveguide-supplied coaxial-line-based nozzleless microwave plasma source (MPS) operated at 2.45 GHz.

1. Introduction

Optical emission spectroscopy (OES) is a very valuable tool in the study of plasma properties (e.g. gas temperature, electron number density) [1]. Gas temperature can often be inferred from the rotational temperature of the heavy species of the plasma [1, 2]. The rotational temperatures in plasmas are often determined comparing experimental and simulated optical spectra. The electron number density in plasma could be obtained from the Stark broadening of atomic spectral lines [1, 3, 4].

Recently, microwave plasma sources (MPSs) operated at atmospheric pressure and high gas flow rates have been developed by us. They found applications in the processing of various gases. Destruction of Freon HFC-134a [5] and production of hydrogen via methane conversion [6] in microwave atmospheric pressure plasmas were reported lately.

In this paper, results of spectroscopic study of microwave plasma at high argon flow rates are presented. The developed coaxial-line-based nozzleless MPS is designed to be used for production of hydrogen via hydrocarbons conversion.

2. Experiment

The experimental setup consisted of: microwaves (2.45 GHz) supplying and measuring system, gas supplying and flow control system, MPS, optical lens and spectrometer with sensitivity calibrated CCD camera and PC computer for spectra analysis. The rotational temperatures of OH radicals were determined by comparing the measured and simulated spectra in LIFEBASE [7] program. Also the method described by Izzara [2], based on analyzing intensities of two groups of unresolved rotational lines of the OH ($A^2\Sigma \rightarrow X^2\Sigma$) band, was used to compare the results. The electron number density in argon plasma was determined using the method based on the Stark broadening of H_β (486.13 nm) spectral line of the hydrogen Balmer series [1, 3, 4].

The MPS was based on a standard WR 430 rectangular waveguide with a section of reduced-height, preceded and followed by tapered sections. The plasma in the form of a flame was generated on the end of a cylindrical electrode which penetrated microwave plasma generator through circular gaps on the axis of the waveguide wide wall and protruded below bottom waveguide wall. The flame was enclosed in a quartz cylinder surrounded by a cylindrical metal shield with a slit for visualization. The working gas was flowing through the internal electrode creating axial gas flow. Nitrogen swirl flow was used as a additional for cooling the quartz tube. The working gas flow rates were between 50 and 200 l/min. Flow rate of the additional nitrogen swirl was 50 l/min. The absorbed microwave power varied from 600 up to 4000 W.

3. Results

Obtained rotational temperatures of OH radicals were from 600 to 1100 K, depending on location in plasma, argon flow rate and absorbed microwave power. The electron number density ranged from $8*10^{14}$ up to $3,6*10^{15}$ cm^{-3}.

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On application of cw external-cavity quantum cascade infrared lasers for plasma diagnostics

D. Lopatik, N. Lang, U. Macherius, H. Zimmermann and J. Röpcke

INP Greifswald, Felix-Hausdorff-Str. 2, 17489 Greifswald, Germany

Mid-infrared laser absorption spectroscopy (MIR-LAS) has been proven to be a versatile diagnostic technique for molecular plasmas. A new class of MIR radiation sources, external cavity quantum cascade lasers (EC-QCL), with a high potential for multiple species detection has been successfully tested for plasma diagnostics purposes.

Tunable diode laser absorption spectroscopy (TDLAS) in the mid-infrared spectral range using lead salt lasers as radiation sources has been proven to be a versatile plasma diagnostic technique. In particular TDLAS is well suited for the measurement of absolute ground state concentrations of a wide variety of molecular species including radicals and molecular ions thereby providing a link with chemical modelling of the plasma. For the simultaneous monitoring of multiple molecular plasma species TDLAS systems, which make use of several lead salt lasers, have been developed in the past [1].

The recent development and commercial availability of pulsed and cw QCLs for wavelengths longer than 3.4 µm and inter-band cascade lasers (ICLs) for shorter wavelength offer an attractive new option for MIR-LAS for plasma diagnostic purposes. Distributed feedback (DFB) QCLs provide continuous mode-hop free wavelength tuning. Their total emission range is typically limited to less than 7 cm^{-1}. Therefore a multi-component detection to study infrared active compounds in reactive plasmas requires, as in the TDLAS case, the combination of several QCLs in a spectrometer [2]. Meanwhile the variety of QCLs and ICLs operating at room temperature are considered as substitutes for cryogenic cooled lead salt lasers, which has led to a rapid development of MIR-LAS from a niche position to a standard diagnostic technique [3].

Recently tunability over much broader spectral ranges than with a typical lead salt laser or DFB-QCL has been achieved using external cavity configurations. Nowadays, EC-QCLs, which are available in pulsed or cw working mode, can be tuned over more than 100 cm^{-1}. Modern cw EC-QCL provide mode-hop free tuning ranges in the order of up to 80 cm^{-1}, at small line width of typically 20 to 60 MHz ($6 - 18 \times 10^{-4}$ cm^{-1}) at power values of up to 150 mW [4]. At present EC-QCLs are used for an increasing number of applications including high resolution isotope analysis, trace gas monitoring and explosive detection. [5, 6].

In the present contribution results of testing cw EC-QCLs as radiation sources for MIR-LAS studies of molecular plasmas will be reported. EC-QCLs have been used for purposes of multiple species detection in microwave plasmas containing hydrocarbons. Figure 1 shows a typical absorption spectrum with absorption features of CH_4, C_2H_2 and HCN. The line shape of the absorption lines has been used for gas temperature determination via Doppler broadening analysis. The power of the EC-QCL has been varied to study possible saturation effects [7].

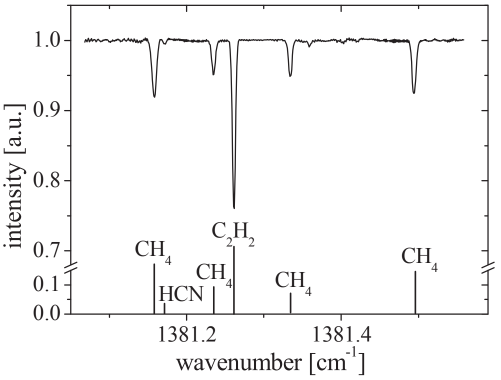

Fig. 1: *Example of absorption spectra of CH_4, C_2H_2 and HCN measured with EC-QCL in an $Ar/N_2/CH_4$ MW discharge by P=0.2 kW and p=0.5 mbar.*

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Ozone production in O_2 plasma at low pressure: evaluation of surface and gas phase mechanisms.

D Marinov[1], O Guaitella[1], V. Guerra[2], N Sirse[1], J-P Booth[1] and A Rousseau[1]

[1]*LPP, Ecole Polytechnique, UPMC, Université Paris Sud-11, CNRS, Palaiseau, France*
E-mail: daniil.marinov@lpp.polytechnique.fr
[2]*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Lisboa, Portugal*

Ozone production in a pulsed O_2 DC discharge in silica reactor at pressures in the range 1.3-6.7 mbar was investigated. Time-resolved *in-situ* measurements of ozone and atomic oxygen concentrations were performed by UV absorption and TALIF. The comparison between the experiment and modelling results reveals that O_3 is formed in the gas phase reaction $O+O_2+O_2 \rightarrow O_3+O_2$ and indicates an important role of vibrationally excited ozone. Moreover, it demonstrates that O_3 production on the reactor walls plays only a minor role in the conditions of this study. Heterogeneous ozone formation was evidenced when high specific surface glass fibres were introduced in the reactor. It was found that the efficiency of ozone formation on the surface increases with increasing the pressure of O_2. At p=6.7 mbar ozone formation accounts for about 25% of the losses of atomic oxygen on the surface of the fibres.

1. Introduction

Ozone production in low temperature O_2 containing plasmas is probably the most studied and the most commercialized plasma chemical process [1]. In low pressure (p~1 mbar) O_2 plasmas, ozone formation is usually neglected due to the low efficiency of the 3 body processes. Recently, it was suggested that ozone production from the surface recombination of oxygen atoms on the reactor walls $(O+O_2)_{wall} \rightarrow O_3$ may represent an important source of O_3 in low pressure O_2 plasmas [2,3]. The aim of this work was to investigate the mechanisms of O_3 production in a pulsed DC discharge in O_2 in the pressure range of 1.3-6.5 mbar. The pulsed discharge technique allows time resolved measurements of O and O_3 kinetics and it is advantageous from the viewpoint of the modelling.

2. Experimental

The experiments were performed in a cylindrical reactor of 60 cm full length and 2 cm inner diameter. The discharge current was in the range of 40-120 mA and the typical pulse duration was 0.5-2 ms. Ozone concentration was measured *in-situ* by broadband UV absorption spectroscopy. The absolute concentration of atomic oxygen and its kinetics in the post-discharge was measured by TALIF. Experiments were done either in a bare silica reactor or with an introduction of high specific surface glass fibres. A self-consistent kinetic model of a pulsed DC discharge in O_2 and its afterglow was developed.

3. Results

Figure 1 shows ozone production as a function of afterglow time at different O_2 pressures. In the same conditions the absolute concentration of O produced during in the discharge was found in the range $(0.5\text{-}1)\cdot 10^{15}$ cm^{-3} . The lifetime of O in the afterglow was 70-160 ms and it decreased with increasing the gas pressure. On the same graph the result of the modelling for 6.7 mbar pressure is shown. Model calculations prove that in the bare reactor, ozone is formed predominantly in the 3-body gas phase reaction and reveal the key role of the excited ozone in the kinetics of O_3 formation.

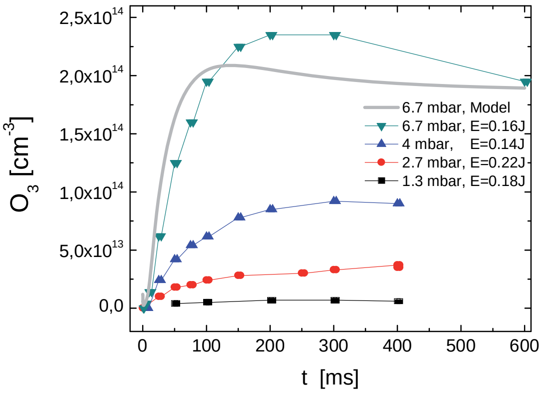

Fig. 1: Ozone production in the afterglow of a pulsed DC discharge at different pressures.

In order to enhance the role of surface processes, a tissue composed of glass fibres was introduced in the reactor. In the presence of the fibres the lifetime of O was 1-5 ms and ozone was formed exclusively on the surface. The efficiency of O_3 surface production was found to increase with increasing the gas pressure. At 6.7 mbar ozone production accounts for 25% of the O surface losses.

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Study of the barrier discharge in argon/acetylene mixture

V. Mazankova , P. Kloc, L. Zajickova, M. Elias

Masaryk University, Department of Physical Electronics, Faculty of Science, Kotlarska 2, 61137 Brno, Czech Republic E-mail: mazankova@fch.vutbr.cz

This work extends our investigation in the field of barrier discharges (BDs) in the mixture of argon with acetylene. The investigation is aimed at understanding of the basic processes in the generated plasma at low and high temperature. Employed methods include optical emission spectroscopy, high speed ICCD camera and electrical properties measurements. The key goal of the experiments is the production of carbon nanotubes in the easily achieved BDs.

1. Introduction

Barrier discharge (BD) is a long known phenomenon. It can be described as a discharge between two electrodes which are separated by at least one dielectric barrier. In wide range of conditions this discharge appears in the form of short duration spatial bounded microdischarges called filaments. The plasma inside one filament can be characterized as low temperature weakly ionized non thermal plasma.

Under some special conditions the discharge can burn in diffuse form with properties similar to the low pressure glow discharge. The required conditions are mainly connected to the used gas, but electrode shape and applied voltage properties also plays important role [1].

2. Experimental Setup

The experimental setup was generally consistent with the one used in [2] with a few modifications. Upper electrode dielectric was replaced by circular one made of quartz ($\varepsilon_r = 3.8$). Even though this new electrode did not allow direct gas pumping from the discharge area, the gas flow through the discharge gap was high enough for our purposes.

A lens was attached to the side window to focus the light from the discharge to optical fibre. The optical emission spectra were measured by Jobin-Yvon HR-1000 spectrometer (2400 gratings/mm) equipped with CCD detector. The lower electrode included a heating device allowing it to be heated up to 1000 K.

3. Results and Discussion

Homogeneity of the discharge was investigated by the means of fast ICCD camera. The obtained results are shown in Fig. 1. The discharge in pure argon was retainimg the form of standard BD with filaments appearing during each half period. With admixture of the acetylene the discharge became diffuse. Upon closer investigation the discharge spatial homogeneity was found not to be ideal across the entire discharge area.

Fig. 1: *ICCD image of the discharge in pure argon (left) and argon with 0.41% acetylene admixture (right). Upper electrode is negatively charged.*

Optical emission spectra as shown in Fig. 2 were obtained from the discharge in pure argon and in argon/acetylene mixture. The argon line intensity drop was observed for acetylene mixture suggesting energy transfer away from argon atoms. Also molecular bands of impurities which were clearly visible in the discharge in pure argon nearly completely disappeared in the mixture.

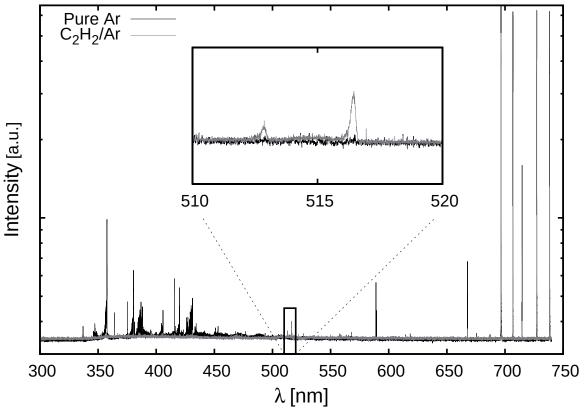

Fig. 2: *Optical emission spectra of discharge in pure argon and with admixture of 0.4 %vol of acetylene.*

Acknowledgement

This work was supported by the Czech Science Foundation under the contract number P205/10/1374.

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Power dependence of the nitrogen pink afterglow effect

V. Mazankova, F. Krcma, I. Soural

Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno Czech Republic
E-mail: mazankova@fch.vutbr.cz

Influence of discharge power on nitrogen DC flowing post-discharge was studied by optical emission spectroscopy in the spectral range of 300–800 nm. The plasma was generated in the quartz discharge tube at pressure of 1 kPa. The applied power was 90–290 W (discharge current was 50–200 mA). The relative populations of $N_2\,(B\ ^3\Pi_g)$, $N_2\,(C\ ^3\Pi_u)$, and $N_2^+\,(B\ ^2\Sigma_u^+)$ states were calculated for post-discharge time up to 50 ms. Results showed a strong applied power dependence of the nitrogen pink afterglow effect.

1. Introduction

Presented work extends our studies with nitrogen post-discharges under different experimental conditions as temperature, pressure, power, presence of various admixtures and reactor wall materials [1]. Relaxation processes of atomic and various very long live molecular metastables created during an active discharge lead to the common thermal equilibrium. These processes are connected with the emission of visible light that can be observed up to one second after switching off the active discharge. Optical emission spectroscopy was used for the presented study that was focused on observation of power influence on relative populations of nitrogen states.

2. Experimental set up

The DC flowing post-discharge was used for the experimental study. The active discharge was created in a quartz discharge tube with a 120 mm electrode distance. Detailed description of the experimental set up was given in [2].

The discharge power was in the range of 90–290 W at total gas pressure of 1 000 Pa. The reactor system was pumped continuously by a rotary oil pump separated from the discharge tube by liquid nitrogen trap. The gas flow was automatically controlled by mass flow controllers, and the total gas pressure in the discharge tube was measured by a capacitance gauge. The optical spectra in the range of 300–800 nm were measured by Jobin Yvon spectrometer TRIAX 550 with the 300 grooves per mm grating coupled with a multichannel detector.

3. Results and discussion

The relative populations of $N_2(B)$, $N_2(C)$ and $N_2^+(B)$ states were calculated from the optical emission spectra. Fig. 1 shows the dependencies of relative populations on decay time for $N_2(B)$ relative population during the post-discharge at three selected applied powers as an example. The dependence shape is more or less the same also for the other studied states. The strong population enhancement can be seen at the decay time of about 5–20 ms that is known as a pink afterglow effect or a short live afterglow, respectively.

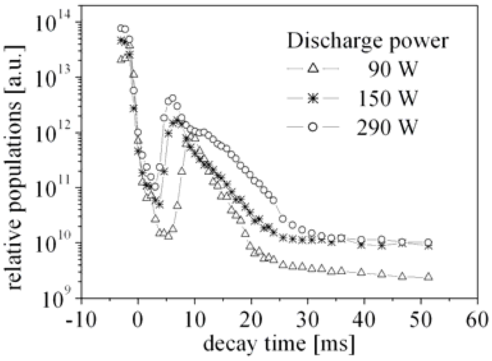

Fig. 1: *Dependencies of relative populations on decay time for $N_2(B)$ state for selected discharge powers.*

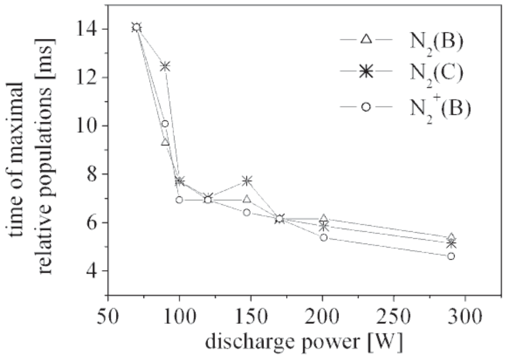

Fig. 2: *Dependencies of time of the maximal relative populations on discharge power*

The afterglow position as well as its maximal intensity is strongly dependent on the applied power as it is demonstrated in Fig. 2. The maximum of populations shifts to shorter decay times with the increasing discharge power. The preliminary experiments have shown that this effect is probably caused by the difference in plasma temperature.

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The response of microcrystalline film growth to changing plasma conditions observed by optical emission and in-situ Raman spectroscopy

S. Muthmann, F. Koehler, M. Meier, R. Carius and A. Gordijn

[1]IEK-5 Photovoltaik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

The composition of the plasma used to deposit microcrystalline silicon is of strong importance for the properties of the growing film. By combining optical emission spectroscopy (OES) and in-situ Raman spectroscopy (IRS) the reaction of film growth on changes of the plasma composition were studied.

1. Introduction

Microcrystalline silicon (µc-Si:H) is a material with increasing importance for photovoltaics. In multi-junction solar cells µc-Si:H is used in combination with amorphous silicon due to the different absorption characteristics of the two silicon configurations [1]. A common method to deposit µc-Si:H is plasma enhanced chemical vapor deposition (PECVD). In this process a mixture of silane and hydrogen is decomposed in a plasma that is generated by a radio frequency discharge. The composition of the plasma as well as the properties of the growing material have to be monitored and controlled in order to obtain optimum device performance [2].

A common way to evaluate the suitability of µc-Si:H for solar cell application is Raman spectroscopy. With this method the crystalline volume fraction of microcrystalline films can be evaluated. A novel setup that enables Raman spectroscopy during the deposition of µc-Si:H allows the estimation of this important material property in-situ [3].

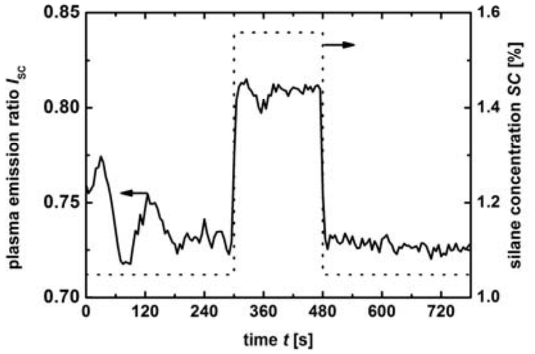

Fig. 1: *Ratio of silane to hydrogen emission (I_{SC}) during a change of the source gas silane concentration (SC)*

2. Experimental Methods

The emission of the PECVD plasma was analyzed using optical emission spectroscopy (OES). By evaluating the intensity ratio (I_{SC}) of a silane line to the hydrogen beta line the silane concentration in the plasma was estimated.

The structural properties of the growing film were determined using a deposition system that was modified to allow in-situ Raman spectroscopy during the deposition of state-of-the-art solar cells. With this experimental setup an accurate estimate of the crystalline volume fraction with a time resolution of roughly 20 s, which corresponds to about 10 nm of film grown during one measurement interval, is obtained.

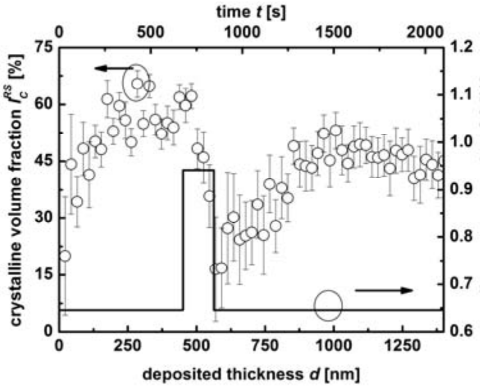

Fig. 2: *Crystalline volume fraction (I_C^{RS})and silane concentration (SC) during the deposition of a microcrystalline layer*

3. Results

In Figure 1 the reaction of the plasma intensity ratio on a change of the silane concentration (SC) in the source gas composition is shown. In contrast to the change in film crystallinity during growth shown in Figure 2 the reaction of the plasma is much faster.

Hence in-situ Raman spectroscopy can be used to improve the understanding of the connection between plasma composition and film growth and improve the control of the µc-Si:H deposition process.

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On laser induced spectroscopy of OH radical applied to an atmospheric RF plasma jet

A. Nikiforov[1], L. Li[1], Qing Xiong [1,2], N. Britun [3], R. Snyders [3], Ch. Leys [1], X. P. Lu [2]

[1] *Department of Applied Physics, Research Unit Plasma Technology, Ghent University, Jozef Plateaustraat 22, Ghent B-9000, Belgium, E-mail:Anton.nikiforov@ugent.be*
[2] *College of Electrical and Electronic Engineering, HuaZhong University of Science and Technology, WuHan, Hubei 430074, People's Republic of China*
[3] *Chimie des Interactions Plasma-Surface (ChIPS), CIRMAP, Université de Mons, 20 Place du Parc, B-7000 Mons, Belgium*
[4] *Materia Nova Research Center, Parc Initialis, B-7000 Mons, Belgium*

Mechanism of laser pumping of OH radicals generated in a radio frequency atmospheric pressure plasma jet operated in Ar with 0.3% H_2O mixture is investigated by time-resolved LIF spectroscopy. The LIF spectrum of OH (0-0) band indicates that the population of the OH rotational molecular states significantly depends on the process of rotational/vibrational relaxation and strong deviation from Boltzmann rotational population distribution of OH(A) is observed within the decay time.

1. Introduction

Atmospheric plasma jets characterized by high concentration of radicals and low gas temperatures are suitable for many applications particularly for modification of sensitive surface [1]. Laser-induced fluorescence (LIF) spectroscopy is a powerful technique that has direct access to the ground state species. Often both species densities and velocity distribution of probed species are derived from the time integrated fluorescence signal. It assumes that the rotational (RET) and vibrational relaxation (VET) processes are fast enough after the laser excitation. In present work time-resolved LIF spectroscopy is used in order to investigate the effect of VET and RET relaxation on time-resolved LIF spectrum of OH radicals and rotational population distribution.

2. Experimental part

The RF (13.56 MHz) plasma jet was sustained in Ar+0.3% H_2O mixture at atmospheric pressure with flow rate of 2 slm. Second harmonic of a Sirah CobraStretch dye laser pumped by SpectraPhysics INDI laser on 355 nm was used to generate the 3 ns laser pulses at 284 nm. The laser beam passed through the plasma jet was fixed at 1 mm above the nozzle. Time resolved two-dimensional cross section of OH fluorescence was detected by an ICCD camera synchronized with the laser pulse. The wavelength resolved fluorescence signal of OH bands (308 nm, 0.03 nm resolution) was detected by Shamrock spectrometer. Transitions $P_1(4)$, $P_2(3)$, $P_2(6)$ of $X^2\Pi$ state of OH radicals were excited by the laser to the vibrational level $v^{'}=1$ of $A^2\Sigma^+$ state.

After the laser pulse at time scale of 20 ns, a strong irradiation around 312-316 nm appears in the LIF spectra which belongs to radiative transition from level $v^{'}=1$ of $A^2\Sigma^+$ to $X^2\Pi$ $v^{''}=1$. At time scale of 20-40 ns after the laser excitation the intensity of the band (0,1) drastically decreases and much stronger band (0,0) starts to dominate all the spectra. The time-resolved LIF spectrum of OH (0-0) band (308 nm) demonstrates that vibrational and rotational relaxation substantially affect the population of OH rotational states at time scale of 150 ns after the laser pulse.

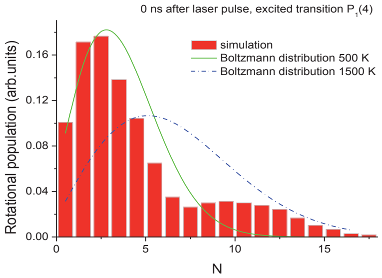

Fig. 1: *Typical rotational populations of OH(A)* ($A^2\Sigma^+$, v '=0) *after the laser excitation.*

At time scale of 50 ns after the laser pulse the vibrational energy transfer mainly due to collisions with Ar results to filling of $A^2\Sigma^+$, v '=0 rotational levels characterized by non-Boltzmann distribution with overpopulation at N'>8, fig.1. The rotational distribution of excited OH radicals at gas temperature of 500 K (measured independently by thermocouple and emission spectroscopy) is only observed at 150 ns after the laser excitation. Correspondingly, time and wavelength integrated LIF signal cannot be considered directly proportional to ground density of OH radicals but it is function of VET and RET processes. Both VET and RET have to be considered carefully especially if LIF signal decay time is used as a parameter for absolute OH density calculations.

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Optical emission spectroscopy of H_α and H_β in a glow discharge mixture of Ar/H_2

P. G. Reyes[1], C. Torres[1], A. Gómez[1], H. Martínez[2].

[1]*Facultad de Ciencias, Universidad Autónoma del Estado de México, e-mail: pgrr@uaemex.mx, Instituto Literario 100, Col. Centro, 50000, Toluca, Estado de México, México*

[2] *Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, P.O. Box 48-3, 62251, Cuernavaca, Morelos, México*

DC glow discharge in a mixture of Ar/H_2 gases is experimentally investigated. Optical emission spectroscopy was used for plasma characterization of the gas mixture glow discharge of Ar/H_2 at a total pressure of 3.0 Torr. The emission intensities of species observed were monitored as a function of wavelength, using a spectrometer in the wavelength range of 200 to 1000 nm. The species observed were H_β (486.1 nm), H_α (656.2nm); Ar^* (750.3 nm)-($1s_2$-$2p_1$); Ar^* (763.5 nm)-($1s_5$-$2p_6$) and Ar^* (811.5 nm)-($1s_5$-$2p_9$).

1. Introduction

The DC glow discharge in a mixture of Ar/H_2 gases have been studied during the last years. The particular interest is the H_α spectral line, which it is widely used in astrophysics for many applications. In addition, interactions, such as quenching collisions between excited Ar and hydrogen molecules, and charge exchange collisions between Ar ions and hydrogen molecules. These processes can play a significant role in the determination of plasma compositions. Among plasma diagnostics techniques, optical emission spectroscopy (OES) allows an identification of reactive species and gives information on the energetic properties of plasma and on plasma processes. The main advantage of OES comparing to other plasma diagnostics techniques is its non-intrusive character. In the present work, we present the results of plasma characterization by optical emission spectroscopy (OES) the Ar/H_2 mixture for different pressure, varying the concentration of each gas to a maximum pressure of 3 Torr.

2. Experiment setup

The apparatus to measure the plasma emission spectrum is identical to that described in previously work [1]. DC glow discharge plasma in a mixture of Ar-H_2 gases was generated in a plasma apparatus of the Advanced Physics Laboratory of de Science Faculty UAEMex.

3. Results

The experimental study mainly focused on the optical emission spectroscopy measurements of the Ar/H_2 glow discharge mixture, varying the concentration of gases. The experiment was realized observing the optical emission from the DC plasma in the wavelength range of 200-1100 nm. It species observed correspond to H_β (486.1 nm), H_α (656.2nm); Ar^* (750.3 nm)-($1s_2$-$2p_1$); Ar^* (763.5 nm)-($1s_5$-$2p_6$) and Ar^* (811.5 nm)-($1s_5$-$2p_9$).

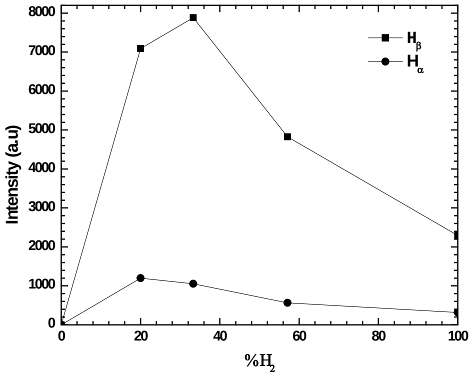

Fig. 1: *Intensity of H_α and H_β vs. H_2 concentrations in a glow discharge mixture of Ar/H_2.*

Figure 1 shows the intensity of the H_α and H_β as a function of the concentration of the gases. It can be seen the intensity of H_β displays a maxima intensity at 33.3% of H_2 in the mixture and the intensity of both lines decreases as the concentration of H_2 is increased. The influence of the Ar in the discharge plays an important rule en the production of both hydrogen lines. The physical effect will be discussed in the conference.

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Acknowledgments

We are grateful to Nayeli Rodriguez Osorio (FC-UAEM) and Anselmo González Trujillo (ICF-UNAM) for her technical assistance. This research was supported by DGAPA IN105010, CONACyT 128714 and student grant Enlace-UAEM.

Intensity changes in time of high-frequency electrodeless discharge lamps containing heavy metals

A. Svagere[1], Z. Gavare[1], J. Skudra[1], M.Zinge[1]

[1]*Institute of Atomic Physics and Spectroscopy, University of Latvia, Skunu street 4, Riga, LV-1050, Latvia E-mail: anda.svagere@gmail.com*

The aim of current study is to investigate the changes of the intensity of atomic lines as well as different admixtures during the operating time of the lamp. In this work we present results of intensity measurements of HFEDLs filled with In+KI+Ar, PbI_2+Ar and BiI_3+Ar.

1. Introduction

High-frequency electrodeless discharge lamps (HFEDLs) are widely used as light sources in different scientific devices, for instance, in atomic absorption spectrometers. These lamps are well suited for the plasma-surface interaction studies as well, since they don't have electrodes. The importance of such plasma-surface interaction studies is determined by the fact that during the lamp operation plasma interacts with the bulb wall material, causing nanoscale modifications of this material, and it is well known that surface topography influences some important properties of the lamp, like operating lifetime. The surface characteristics become especially important when decreasing the dimensions of the light source.

Surface modifications can be affected by the excitation field frequency and plasma temperature, as well as by plasma composition [1]. Different impurities in plasma can induce changes on the inner surface of the lamp, too.

The aim of current study is to investigate the changes of the intensity of atomic lines and emission of different admixtures during the operating time of the lamp. In this work we present results of intensity measurements of HFEDLs filled with In+KI+Ar, PbI_2+Ar and BiI_3+Ar.

2. Experimental part

The plasma under study was several HFEDLs filled with (1) In+KI+Ar, (2) PbI_2+Ar and (3) BiI_3+Ar. The buffer gas pressure was 3 Torr.

The HFEDL vessels are made of SiO_2 glass and filled with working element and argon at low pressure. The inductively coupled discharge is induced by placing the lamp in electromagnetic field with frequency of 100 MHz.

The HFEDLs were operated for about 5-6 hours at particular value of excitation generator voltage (in the range from 20 to 30 V), and the emission spectra changes in time were analyzed. The emitted light spectra were registered using spectrometer JobinYvon SPEX 1000M (grating 1200 $l \cdot mm^{-1}$, focal length 1 m) with charge-coupled device matrix detector (2048×512 Thermoelectric Front Illuminated UV Sensitive CCD Detector, Simphony).

It was observed that in some cases one could register presence of different chemical compounds like OH, NH, N_2 or CN. The emission intensity changes of such admixtures were registered during the operating time of HFEDL.

3. Results and conclusions

In emission spectra of PbI_2+Ar and BiI_3+Ar HFEDLs different chemical compounds could be registered, for instance, in the spectra of BiI_3+Ar lamp we could observe CN, OH and NH emission, but in spectra of PbI_2+Ar lamp N_2 spectrum could be identified. However, in emission of In+KI+Ar lamps it was not possible to observe emission of any admixtures apart from the working element and buffer gas.

During the lamp operating time of about 5-6 hours, the emission intensity of different admixtures decreased; however the plasma temperature (~900 K) didn't change significantly, as well as emission intensity of atomic lines of working element and buffer gas.

The presence of different chemical compounds in the emission of plasma can be explained as follows. The constituents of such compounds (C, H and N atoms) could have found their way into plasma vessel from the air and grease used in the manufacturing process of the HFEDLs, and then during the plasma discharge they formed different compounds, emission of which then can be registered.

Acknowledgment

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Combination of FTIR spectroscopy and GC-FID+MS to elucidate toluene reactivity induced by non-thermal plasma at ppb levels.

F. Thevenet[1,2], P. Gravejat[1,2], L. Sivachandiran[1,2,3], O. Guaitella[2,3], A. Rousseau[2,3]

[1] *Université Lille Nord de France, F-59000, Lille, France.*

[2] *Département Chimie et Environnement, Ecole des Mines de Douai, F-59508, Douai, France.*

[3] *Laboratoire de Physique des Plasmas, Ecole Polytechnique, UPMC, Université Paris Sud 11, CNRS Palaiseau, France.*

This work aims at characterizing by FTIR and Mass Spectrometry the species produced and the process efficiency during non-thermal plasma treatment of toluene close to indoor air conditions: (i) ppb level concentrations; (ii) in the presence of moisture.

1. Context

Advanced oxidation techniques, and among them Non-Thermal Plasma (NTP), are developed to achieve indoor air treatment of volatile organic compounds (VOCs). Numerous studies investigate the oxidation of a large diversity of VOCs. In these studies, initial concentrations of model VOCs mainly range from 1 to 1000 ppmv. Moreover, experiments are generally performed under dry air conditions. Nevertheless, indoor air is characterized by total concentration of VOCs lower than 500 ppb and relative humidity from 30 to 70 % [1]. The mismatching between experimental conditions reported in papers and the reality of indoor air can be balanced by appropriate analytical devices enabling gas phase characterization at ppbv levels. This approach has already been efficiently conducted with photocatalysis [2] but not with NTP yet.

The objective of this work is to investigate the oxidation of a model VOC by NTP close to real indoor air conditions: (i) determination of toluene conversion rates; (ii) characterization of reaction intermediates; (iii) quantification of mineralization.

2. Experimental

Toluene was selected as a model VOC since it is included into standards for air treatment system qualification. Two analytical devices were combined downstream the NTP reactor:

2.1 Organic species were identified and quantified using gas chromatography (GC) equipped with a flame ionisation detector (FID) coupled with a mass spectrometer (MS). Identification of species downstream the reactor was performed by MS. Quantification was performed by FID. Experimental detection limits of FID on monitored organic compounds are lower than 0.1 ppbv.

2.2 Inorganic species were identified and quantified using FTIR spectrometer equipped with a heated 10m optical path cell and a MCT detector. Detection limits of CO and CO_2 are respectively 76 and 10 ppbv.

2. Results

First, injected power has been varied from 0.1 to 1.6 W. Toluene conversion rate subsequently increased from 70 to 95%. Sixteen gaseous reaction intermediates (RI) have been identified under dry conditions. They are mainly oxygenated aromatic compounds and oxygenated VOCs, but toluene oxidation is not the single reaction pathway. Indeed, five RI contain nitrogen in their structure, indicating significant reactivity between organic compounds and N_2. Moreover, three anhydrides were identified; they are attributed to organic fragment recombination under plasma activation.

Fig. 1 reports the reaction carbon balance (CB) calculated for various input powers. The main effects of input power increase are: (i) increase of identified RI contribution in the CB; (ii) decrease of unidentified RI in the CB; (iii) improvement of the mineralization from 8 to 50% of the CB.

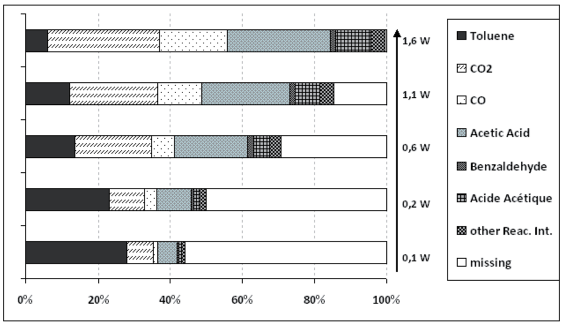

Fig. 1: *Contribution of Toluene, CO, CO_2 and reaction intermediates in the carbon balance for various NTP input powers.*

Secondly, the influence of air relative humidity has been investigated (50% RH i.e. 23 000 ppmv). The presence of moisture reduces from 16 to 8 the diversity of identified RI. 50% RH mainly hinders anhydride formation and the reactivity with N_2 evidenced under dry conditions. Besides, moisture simultaneously promotes (i) carboxylic acids formation, (ii) mineralization, (iii) and especially CO_2 selectivity.

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Measurement of OH concentration by laser-induced fluorescence in an atmospheric RF plasma jet.

J. Voráč[1,2], V. Procházka[1], P. Dvořák[1]

[1] *Masaryk University, Faculty of Science, Dep. of Physical Electronics, Brno, Czech Rep.*
E-mail : 1752822mail.muni.cz

[2] *ZIK-Plasmatis, INP Greifswald e.V., Felix-Hausdorff-Str. 2*
17489 Greifswald, Germany

A method for measuring the absolute concentration of OH radicals by laser-induced fluorescence in atmospheric pressure plasma without knowing the concentration of the collision partners is suggested. A scheme using the lowest vibrational states is used to avoid the problems with vibrational energy transfer. Rotational energy transfer was found to be extremely fast and thus rotational thermal equilibrium is always assumed.

1. Introduction

OH radical has been in the scope of scientists for a long time, because it allows tracking important chemical processes. It is also expected to play an important role in the plasma material processing and the interaction of plasma with living cells.

2. OH Density Measurement with LIF

The group in Bielefeld have come with an easy-to-use simulation environment LASKIN [1]. This allows to take into account electronic quenching, rotational and vibrational energy transfer (RET and VET), but one needs to know the relative densities of collision partners. Another appreciable contribution to understanding the LIF of OH radical was brought by Crosley and Luque and their program LIFBASE [2].

Based on their results, we have tried to develop a method that would work even if the composition of plasma is not known.

We are using the excitation from $X^2\Pi$ ($v'' = 0$) into rotational sub-states of $A^2\Sigma^+$($v' = 0$) and observe the fluorescence in the same transition. That allows us to avoid VET, since the vibrational temperature of our discharge is low and the upper vibrational states are not significantly populated. Typical fluorescence lifetime is >100 ns, whereas the laser-pulse is <10 ns. allows us to avoid the scattered laser light by starting the acquisition after the laser pulse has ended.

Spectrally and time-resolved measurements show, that the RET is very rapid and straight after the end of the laser pulse, the rotational distribution of the upper state is in rotational thermal equilibrium.

3. The Plasma Pencil

In the past, the Plasma Pencil was successfully used to remove dirt and corrosion from archaeological findings and changing the surface energy of various materials [4].

The plasma pencil is a nozzle driven at 13.56 MHz used with argon as a working gas [3]. The OH radicals are generated from the humidity in the ambient air and in the gas-leading pipes.

Also the influence of parameter variation (working gas flow rate and driving rf power) on the OH density is studied.

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Infrared gas phase studies in air-like atmospheric pressure DBDs

S. Welzel[1], S.A. Starostin[2], H. de Vries[2], M.C.M. van de Sanden[1,3], R. Engeln[1]

[1]*Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands E-mail: s.welzel@tue.nl*
[2]*FUJIFILM Manufacturing Europe B.V., P.O. Box 90156, 5000 LJ Tilburg, The Netherlands*
[3]*Dutch Inst. for Fundam. Energy Research (DIFFER), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands*

The effluent of an industrial roll-to-roll reactor for synthesising silica-like barrier layer using atmospheric pressure (glow) discharges has been studied by means of *ex-situ* FT-IR spectroscopy. The focus of this study was on etching conditions in air-like gas mixtures without precursor. Particularly, HCOOH was found to be a good indicator for etching conditions present during foil treatment. Additionally, a distinct N_xO_y chemistry will be discussed.

1. Introduction

Diffusive dielectric barrier discharges (DBDs) at atmospheric pressure have been shown to be a promising tool in large-area plasma-enhanced chemical vapour deposition (PE-CVD) [1,2]. Excellent SiO_2-like barrier layers on polymeric substrates have been obtained through PE-CVD in a roll-to-roll mode in cost-efficient air-like gas mixtures of $Ar/N_2/O_2$ [2]. Different regimes of plasma-polymer interaction along the electrodes have been identified which are mainly characterised by a competition between deposition and etching processes [3] Complementary gas-phase studies using infrared (IR) absorption spectroscopy are reported focusing on precursor-free gas mixtures to mimic an etching regime of the polymer.

2. Experimental

Given the challenging optical access to small gap (0.5 mm) DBDs in general and to the industrial roll-to-roll configuration in particular an *ex-situ* approach was chosen. A gas sampling system was implemented which collected continuously a fraction of the effluent into a multi-pass absorption cell. A high-resolution Fourier-Transform IR (FT-IR) spectrometer was aligned to the sampling cell to yield 7 m total absorption path at reduced pressure. The discharge was operated in diffusive mode in gas mixtures of air/Ar (15/1 slm) and O_2/Ar (0..2/1 slm), respectively. To distinguish gas phase species produced from etching of the PEN substrate several experiments were carried out with a polymeric substrate pre-deposited with a SiO_2 protecting layer.

3. Results

A (differential) survey spectrum (fig. 1) reveals the main (stable) gas phase components: apart from NO (d), NO_2 (c) and N_2O (f) carbon containing species such as CO (e), CO_2 (g) and formic acid (HCOOH, b) are detected. Additionally, HONO (a) is usually present whereas other typical components in air-like DBDs such as N_2O_5, HNO_3 and O_3 are usually not identified in the spectra.

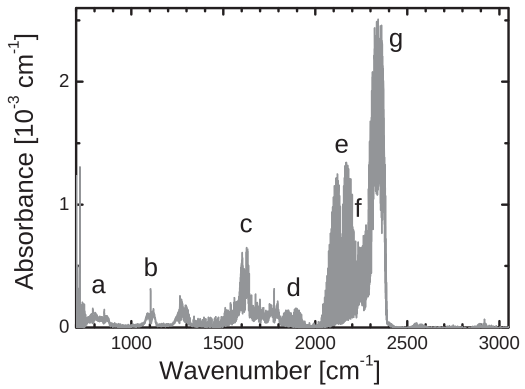

Fig. 1: *Typical FT-IR survey spectrum from the effluent of an air-like DBD. Carbon containing species such CO (e), CO_2 (g) and HCOOH (b) indicate the etching of the polymer.*

From the analysis of the gas phase composition it can be concluded that a chemistry similar to de-NO_x processes, i.e. N_xO_y chemistry in the presence of trace amounts of hydrocarbons, is observed. This leads to quenching of reaction channels which would form N_2O_5 or HNO_3. On the other hand, HCOOH is produced and turns out to be a good indicator for dominant etching conditions in the discharge. Additionally, the O_3 generation is hampered due to the poisoning of the process.

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SESSION 3

Tuesday 15th, 9h00

NICE-OHMS – A Frequency Modulated Cavity Enhanced Spectroscopic Technique for Detection of Gases down to the 10^{-12} cm^{-1} Hz$^{-1/2}$ Range

Ove Axner,* Patrick Ehlers, Isak Silander, and Junyang Wang

Department of Physics, Umeå University, S-901 87 Umeå, Sweden,
**E-mail: ove.axner@physics.umu.se*

Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) is a laser-based spectroscopic technique originally developed for high precision frequency standard applications at JILA in Boulder, CO, USA, with unique properties. By combining an external cavity for increased interaction length with the sample with frequency modulation for reduced influence of noise, the technique achieves an extraordinary high sensitivity. In addition, by choosing the modulation frequency equal to the free-spectral range of the cavity, the technique obtains an immunity to laser frequency noise, which implies that detection can be made as if the cavity would not be there. Finally, both Doppler-broadened and Doppler-free signals can be measured in either absorption or dispersion mode of detection. In its first realization, based on a well stabilized solid state laser, an impressive absorption sensitivity of 10^{-14} cm^{-1} was demonstrated for molecular species detection.[1] This is several orders of magnitude better than any other optical detection technique can achieve, which gives NICE-OHMS a large potential for sensitive trace gas analysis.

However, the technique has, for a long time, been considered too complex to be used for practical trace gas analysis. To make the technique more applicable to trace gas detection, our research group has challenged this and is developing the NICE-OHMS technique further, with the main aim of reducing the complexity of the instrumentation while keeping as much as possible of the high sensitivity.[2] The systems developed so far are based upon narrowband fiber lasers, as well as a narrowband DFB laser, and have, whenever possible, utilized fiber-coupled components for a more compact realization. Using C_2H_2 as the pilot species, we have scrutinized the dependence of the technique on a variety of parameters for optimum sensitivity, selectivity, and thereby its applicability. Using a cavity with a finesse of 5700, we have presently demonstrated an absorption sensitivity of 5.6×10^{-12} cm^{-1} Hz$^{-1/2}$, or $\Delta I / I$ of 7.2×10^{-11} over 10 sec, which allows detection of low ppt concentrations of acetylene in atmospheric samples.[3] The talk will provide a short description of the basic features of the technique and some of the most important results.

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Gas temperature and NO density measurements in atmospheric pressure plasmas

AFH van Gessel, PJ Bruggeman, JJAM van der Mullen

Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
E-mail: a.f.h.v.gessel@tue.nl

Optical emission spectroscopy and laser induced fluorescence are applied to an atmospheric pressure microwave plasma jet of helium and air. The LIF spectra are time and wavelength resolved, and are used to determine the rotational temperature, and absolute density of nitric oxide. A comparison is made to the rotational temperatures found by OES, and detailed motivation of these temperatures as the gas temperature is given.

Atmospheric pressure plasmas are studied for their applications in biomedicine, for example wound healing and bacteria inactivation. Nitric oxide (NO) produced by the plasma is believed to play a major role in many processes in living cells. We studied this NO production in an atmospheric pressure plasma jet, by means of passive and active spectroscopy. We compared two methods: Optical Emission Spectroscopy (OES), and Laser Induced Fluorescence (LIF). By measuring rotational spectra, we are able to determine the temperature and density of NO.

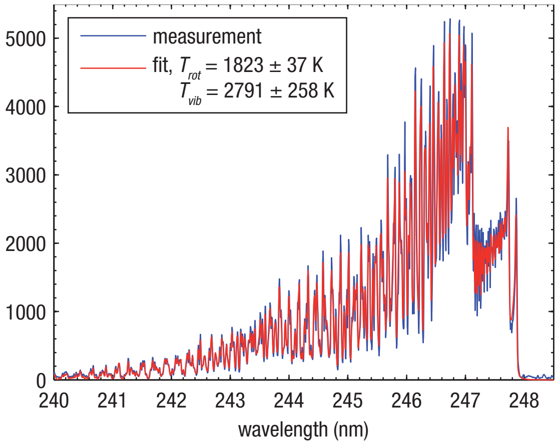

Fig. 1: *Rotational spectrum of NO, measured by optical emission spectroscopy.*

Our plasma source is a microwave jet, flushed with a mixture of helium with 3% air, in an open air environment [1]. We applied OES to determine the rotational spectrum of the NO $A\,^2\Sigma - X\,^2\Pi$ $(v = 0-2)$ vibrational band. The partly resolved spectrum is fitted to determine the rotational temperature (see for an example figure 1).

LIF is applied using a high repetition rate dye laser system (around 226 nm at 4000 Hz) to excite the NO $X\,^2\Pi - A\,^2\Sigma$ $(v = 0-0)$ transition. The fluorescence is measured with a monochromator and a photomultiplier which is connected to a multi channel scaler. This system allows us to measure the rotational LIF spectra wavelength resolved (used to determine the rotational temperature) and simultaneously time resolved (used to determine the quenching).

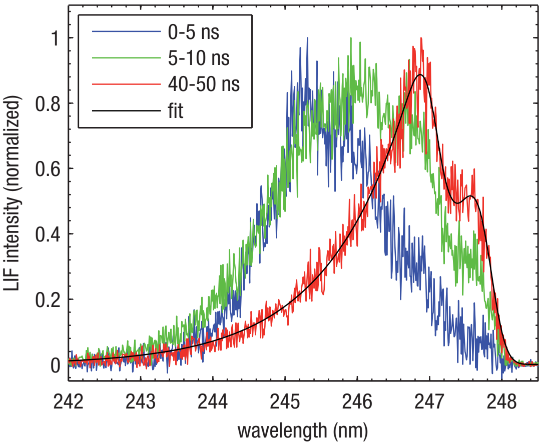

Fig. 2: *Rotational spectrum of NO, measured by laser induced fluorescence. The laser excitation is done at high rotational number ($J = 33.5$). The graphs show the signal measured at different time delays after the laser pulse. The fitted rotational temperature after* 40 *ns is* 1482 ± 52 *K.*

The rotational temperatures found by OES and LIF differ, which could be explained by the time it takes for the thermalization of the non-thermal rotational distribution caused by the production mechanism of the excited state (both by plasma processes or laser), see e.g. [2]. The time and wavelength resolved spectra allow us to visualize the rotational energy transfer, an example of which is shown in figure 2.

The absolute density of NO X ground state is determined by calibrating the LIF signal with a known density of NO. We found spatially resolved densities, in the order of 20 ppm inside the plasma, and an increase in the afterglow.

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Diagnostics of Atomic Oxygen in O_2/Rare Gas Mixture Plasma with Vacuum Ultraviolet Laser Absorption Spectroscopy

K. Takeda[1], M. Hori[1,2]

[1]*Guraduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya Japan, 464-8603*
E-mail: ktakeda@nuee.nagoya-u.ac.jp
[2]*Plasma Nanotechnology Research Center, Nagoya University, Furo-cho, Chikusa-ku, Nagoya Japan, 464-8603*

Absolute densities of $O(^1D_2)$ in O_2 surface-wave-excited plasmas (SWP) with high Kr or Ar dilution were measured by tunable vacuum ultraviolet laser absorption spectroscopy. The behaviors of $O(^1D_2)$ densities were almost same, however, the absolute $O(^1D_2)$ density in the Ar mixture plasma was higher than that in the Kr mixture plasma. From these results, the O_2/Ar SWP had a potential to supply the larger amount of $O(^1D_2)$ density to samples than the O_2/Kr SWP.

1. Introduction

Plasma oxidation is essential for nano and micro fabricating on silicon technology. Because the plasma oxidation has a potential to realize much lower temperature processes compared with thermal oxidation. Therefore, the plasma oxidation has been frequently used in the industry and investigated to achieve higher performance. It has been reported that the O_2 surface wave plasma (SWP) with high Kr gas dilution, has the potential to realize a higher silicon oxidation rate and high-quality silicon oxidation films than other O_2 plasmas.[1] In these processes with the O_2/Kr SWP, it is supposed that the high performance of plasma oxidation would be realized by the oxidizing of atomic oxygen in the excited state ($O(^1D_2)$) generated efficiently by the O_2 dissociation due to metastable Kr* collision in high Kr diluted condition (around 97%).[2] However, in our previous study, from estimation of generation rate of $O(^1D_2)$ in the O_2/Kr SWP on the basis of plasma diagnostics results, it was found that the electron impact was a main process to generate the $O(^1D_2)$ in the O_2/Kr SWP.[3] In this study, a quantitative study on the $O(^1D_2)$ in the O_2 SWPs with Kr or Ar mixture was carried out by tunable vacuum ultraviolet laser absorption spectroscopy (VUVLAS).

2. Experimental setup

The plasma oxidation reactor for the 8 inch wafer with a SWP was used to investigate the behavior of at $O(^1D_2)$ in this study. O_2 and rare gases mixtures were employed as discharge gas. Microwave (2.45 GHz) was applied to the antenna on the quartz plate to generate the SWP. Total pressure and microwave power were density fixed at 1 Torr and 1.2 W/cm^2. The absolute $O(^1D_2)$ densities in the O_2/rare gas mixture SWP were measured by VUVLAS. The VUV laser radiations around the transition lines of 3s $^1D^\circ$-2p $^1D_2$ at 115.22nm for the measurements of absolute densities of $O(^1D_2)$ were generated by the phase-matched frequency tripling in the Xe (40 Torr) and Ar (80 Torr) mixture.

3. Results

Figure 1 shows the dependence of absolute $O(^1D_2)$ densities on the flow rate ratio of O_2/(rare gas+O_2). The flow rate ratio was changed from 0.2 to 40%. In the case of Ar/O_2 SWP, the absolute density of $O(^1D_2)$ increased from 4.3×10^{10} to 1.8×10^{12} cm^{-3} with decreasing the total flow rate ratio up to 1%. And then that of $O(^1D_2)$ slightly decreased from 1.8×10^{12} to 1.0×10^{12} cm^{-3}. The behavior of $O(^1D_2)$ in the O_2/Kr SWP was almost same. However, the absolute $O(^1D_2)$ density in the Kr mixture plasma was 1.2×10^{12} cm^{-3} at O_2/(Kr+O_2) flow rate ratio of 1% and lower on all flow rate ratio condition compared with that in the O_2/Ar SWP. The rate constant for collisional quenching of $O(^1D_2)$ by Kr is around ten times higher than that by Ar. Therefore, it is considered the $O(^1D_2)$ density in the O_2/Kr SWP was lower than in the O_2/Ar SWP. From these results, we confirmed that the O_2/Ar SWP had a potential to supply the $O(^1D_2)$ compared with the O_2/Kr SWP.

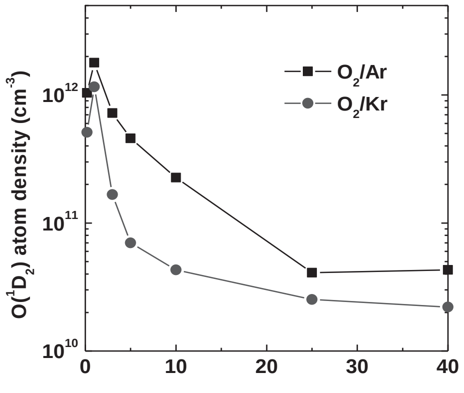

Fig. 1: *Absolute density $O(^1D_2)$ as a function of O_2/(rare gas +O_2) ratio.*

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Time-resolved optical emission spectra of nanosecond discharge in water

I. Marinov[1], O. Guaitella[1], A. Rousseau[1] and S. Starikovskaia[1]

[1]*LPP, Ecole Polytechnique-91128 Palaiseau, France E-mail: ilya.marinov@lpp.polytechnique.fr*

Shadowgraphic and spectroscopic analysis with 2 ns time resolution of underwater nanosecond discharges is presented. Optical emission spectra of positive streamer in water demonstrate hihgly broadened atomic Hα and OI(777nm) line profiles.

1. Introduction

Electrical discharges in water and other dielectric liquids have been extensively studied since almost fifty years, however the mechanism of discharge initiation and propagation is still disputable. The proper measurement of plasma parameters is necessary to calibrate existing models of underwater discharge. The experimental techniques developped for meausrement of electronic density (Ne) and temperature (Te) in gas phase discharges can not be easily applicable in liquids. Optical emission spectroscopy (OES) seems to be a promissing tool for studying electrical discharge in liquid phase [1]. Profiles of emission Balmer lines are very sensitive to the presence of macro- and microscopic electrical fields and are extensively used for determination of Ne and Te in laboratory and interstellar plasmas[2].

2. Experimental setup

Experimental setup is described in detail in [3] and consists of a classical shadowgraph scheme with a Xe flash lamp as a backlight source, an objective producing the parallel beam, imaging lens, beam splitter and two iCCD cameras (ANDOR iStar 734). Time-resolved spectroscopic study is performed with a Shamrock SR-303i spectrometer equipped with a 600 l/mm grating. Discharge device has a poin-to-wire geometry with nickel pin electrode of ~1 µm and interelctrode gap of 2 mm. Plasma is generated by nanosecond high voltage pulser with a 5 ns rise time, 30 ns duration (FWHM) and 10 kV amplitude (FID GmBH). Experiments are carried out in 50 ml quartz optical cell.

3. Results

Single streamer discharge is obtained at 6 kV of applied voltage propagating to the maximal length of 300 µm. Expansion of the discharge channel is measured with the help of two iCCD cameras during the streamer formation phase and in the post-discharge. Analytical model of cylindrical cavity expansion in nonviscous incompressible liquid is applied to get pressure evolution inside the discharge channel. Figure 1.a demonstrates an exponential decay of discharge pressure from 1.3 GPa at 5 ns after ignition to 0,2 GPa at the end of applied voltage pulse. Time-resolved spectrum shows a strong broadening of Balmer lines with almost continuum emission in the region 300-700 nm and weak broadened OI(777nm) line. The best fit of Hα profiles is obtained as a sum of two lorentzian functions. Figure 1.b demonstrates temporal evolution of HFHM for each component of Hα two-lorentzian fit. Since Stark and pressure broadening can be treated independently and both have lorentzian profile, one may suggest that complex Hα line profile is due to the combined contribution of Van Der Waals and Stark broadening. Analysis of Hβ and Hγ profiles are now in progress.

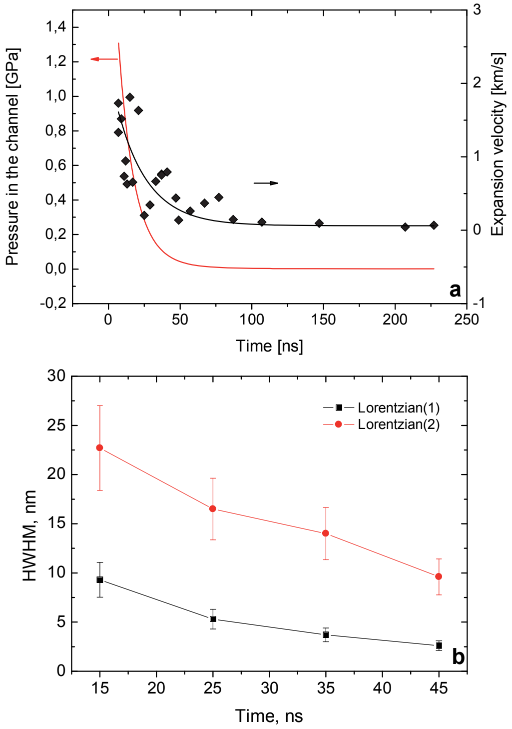

Fig. 1:*a) Pressure in discharge channel b)HWFM of Hα two-lorentzian fit*

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Plasma chemical gas phase processes in plasma polymerization

D. Hegemann[1], B. Hanselmann[1], R. Deradjat[1,2], M. Drabik[1]

[1]*Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St.Gallen, Switzerland*
[2]*Ruhr University Bochum, Institute for Theoretical Electrical Engineering, 44801 Bochum, Germany*

The plasma chemical reaction pathway yielding plasma polymer growth consists of multistep reactions taking part in the gas phase and at the surface. New insights are gained by comparing mass deposition rates under varying energetic conditions with optical emission spectrometry.

1. Introduction

Plasma polymerization is activated by electron excitation in the gas phase yielding different fragments of different numbers and reactivities [1]. Further steps finally yielding film growth might involve plasma chemical gas phase reactions and reactions at the growing film surface. Considering the number of collisions in the gas phase and energetically favourable reactions at the surface, it appears reasonable to assume that most chemical reactions are taking place at the surface [2]. Plasma diagnostic methods such as mass spectrometry (MS) and optical emission spectrometry (OES) tend to observe (stable) species that do not contribute to film growth.

2. Approach

2.1. Macroscopic kinetics

In order to gain more insights into plasma polymerization processes, we therefore developed a (macroscopic) concept based on the energy input both into the gas phase (plasma) and during film growth (surface) that helps to distinguish between predominating gas phase or surface processes [3].

A well-defined reactor geometry was used allowing reliable plasma conditions over a broad parameter range concerning power input *W* and gas flow *F*. By measuring excitation voltage of the RF discharge and electron density, the mean ion energy and the ion flux incident at the substrate surface can be estimated yielding the energy density deposited into the growing film, i.e. the energy flux per deposition rate [4]. Moderate energy densities induce crosslinking, while higher values promote ion-induced effects such as etching.

2.2. Results

Typically, an increase in (mass) deposition rate is obtained by increasing the reaction parameter *W*/*F*, which shows quasi-Arrhenius behavior, followed by a drop in film growth at higher specific energy input. To analyze plasma chemical and physical influences, different experimental series using gas mixtures of CO_2/C_2H_4 were performed at different gas flows. Thereby, the same range of *W*/*F* can be maintained at different energy flux to the substrate. As a result it was obtained that CO_2/C_2H_4 discharges show a transition that is dominated by plasma chemical processes (Fig. 1).

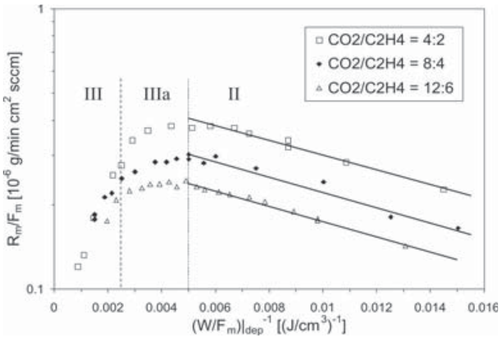

Fig. 1: *The change in deposition rate in regime IIIa is caused by a change in the plasma chemical reaction pathway, since it occurs at fixed W/F independent of the different ion bombardment conditions.*

Using OES, it was investigated whether this transition is accompanied by a change in the gas phase composition of reactive species such as CO, O, H and, CH.

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Study of the optical thickness of laser induced plasma for improved material analysis via laser-induced breakdown spectroscopy

M. Cirisan[1], M. Cvejic[2], J. Hermann[1], S. Jovicevic[2], N. Konjevic[3]

[1]*LP3, CNRS – Université Aix-Marseille, Marseille, France*
[2]*Institute of Physics, University of Belgrade, Belgrade, Serbia*
[3]*Faculty of Physics, University of Belgrade, Belgrade, Serbia*

In order to improve the precision of calibration-free laser-induced breakdown spectroscopy (LIBS) measurements, the existing database of Stark parameters needs to be significantly expanded. In this work, we have studied the optical thickness of laser induced plasma for several Al II lines to be used for LIBS plasma diagnostics.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an emerging technique used for quantitative elemental analysis of materials. Driven by the technological development of pulsed lasers, compact and high-performance spectrometers and detectors, LIBS is a promising “tool” for applications in many areas, such as quality control in industrial production, material recycling, environmental survey, interplanetary exploration etc. Even though the LIBS ability of performing precise analysis has been demonstrated for a significant number of materials, quantitative measurements are still difficult in many cases. This low precision is mainly due to the difficulty of calibrating LIBS measurements.

Calibration-free LIBS measurements procedure, developed in LP3, allows determination of the materials elemental composition by comparing the measured intensities of atomic spectral lines to the spectral radiance of plasma that is generally supposed to be in local thermal equilibrium [1]. The absorption coefficient $\alpha(\lambda)$, used for the calculation of plasma spectral radiance, takes into account the dominant spectral line broadening mechanisms. In order to achieve high precision of calibration-free LIBS measurements, a large database of Stark parameters needs to be available. The amount of Stark parameters data existing in the literature is very limited and they are often imprecise.

2. Study of the optical thickness

By employing optical emission spectroscopy to laser induced plasma one may measure Stark parameters of the spectral lines of any element present in the irradiated sample. Still, one should pay attention not to make erroneous measurements. Laser induced plasma is in most cases very dense, and for a number of spectral lines the plasma is optically thick. Self-absorption may lead to distortion of the spectral line profile, thus producing an apparently large line halfwidth and introducing a large error in the measured value of the Stark halfwidth coefficient [2]. This is why every spectral line needs to be checked on self-absorption, before proceeding to intensity and Stark halfwidth measurement.

In this work, we have employed the method of duplicating the optical path through plasma with a spherical mirror [2] in order to check the optical thickness of laser induced plasma for several Al II lines. Laser ablation of Al alloy was performed using a Nd:YAG laser (5 ns pulse duration, 266 nm wavelength, 3 mJ energy per pulse) in Ar at 50 mbar. This method enables us to quickly verify if the observed spectral line is self-absorbed. Measured values of plasma transmission coefficient, presented in Fig. 1, indicate the presence of self-absorption for three Al II lines. The experimental results are compared to the spectrum calculated using calibration-free LIBS procedure [1]. Furthermore, temporal evolution of the plasma transmission coefficient has been studied for all observed Al II lines in order to find the optimal conditions for Stark halfwidth measurements.

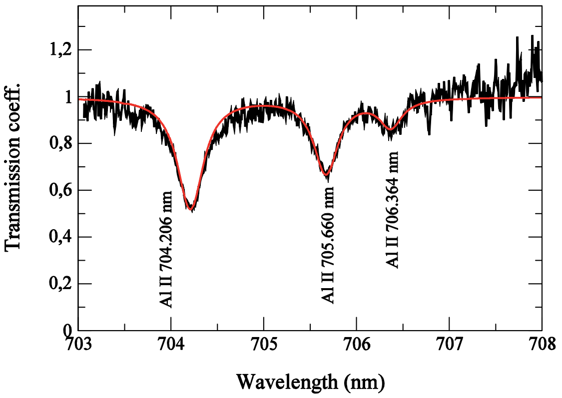

Fig. 1: *Plasma transmission coefficient for three Al II lines.*

Finally, Stark halfwidths have been measured for the Al II spectral lines for which favorable optically thin plasma conditions have been found.

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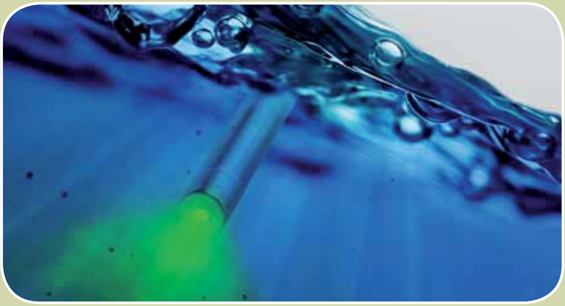
SESSION 4

Tuesday 15th, 16h00

broad spectra fiber solutions

FIBER SPECTROSCOPY from UV to Mid IR-range for PROCESS CONTROL

art photonics



art photonics GmbH was started in Berlin in 1998 with the vision to become the leader in specialty fiber optics of broad spectral range from 180nm to 18µm. **art photonics**' staff with a combined 120 year experience in design and production of fibers, fiber cables, bundles and fiber spectroscopy probes is always keen to meet customer´s expectations in various applications.

Pioneering development of Polycrystalline IR-fiber technology based on extrusion of Silver Halide crystals enables **art photonics** to become the leader in production of unique PIR-fibers – expanding the transmission limit of traditional fiber optics from 2.5µm up to 18µm. PIR-fiber optics enables to use process-spectroscopy in Mid IR spectral range – known as a “finger-print” for molecular vibration absorption bands used in spectral media analysis.

In 2011 **art photonics** has launched new product line **FlexiSpec™** – for **flexible** fiber **spectroscopy** solutions from UV to Mid IR-range. **FlexiSpec™** family includes immersion ATR and transmission probes, fluorescent and diffuse reflection probes - all compatible with any FTIR, FT-NIR or dispersion spectrometer, process-photometer, IR-LED or QCL spectral sensor to used in-line for PAT-applications.

FlexiSpec™ probes design is cleanable for many processes where probe optics can be contaminated by media. Industrial probes are compatible with process-interfaces SensoGate-FOS and Ceramat-FOS with approved fittings to secure their semi or full automated use in complete process control systems. They can be retracted, cleaned and calibrated during chemical process – to enable remote process-control in any liquid, gas or solid mixtures under harsh environmental conditions.

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Cavity enhanced with optical feedback using QCL lasers: Trace analysis at ppt levels in the mid-infrared range

D. Romanini[1]

[1] *Laboratoire de Spectrométrie Physique-CNRS URA 08, Université J. Fourier/Grenoble, B.P. 87-38402 Saint Martin d'Hères Cedex, France*

This work presents recent progress achieved using a cavity enhanced absorption spectroscopy (CEAS) technique which relies on optical feedback (OF) to optimize injection of a high finesse cavity by a semiconductor laser, such as a diode laser or a quantum cascade laser (QCL).

General

While OF-CEAS has about the same performance as Cavity Ring Down Spectroscopy when applied in the near IR region, it has the advantage of a simpler optical setup. Other advantages are the high signal levels which are recovered at cavity output, and the high precision of the spectral data points which are taken on the grid of the high finesse cavity modes.

OF-CEAS has proved to work well with QCL lasers, allowing to access stronger molecular transitions in the mid-IR region, hence improving by several decades the detection limits. On the other hand the high cavity injection efficiency becomes a real advantage at longer and longer wavelengths where optical detectors are less and less sensitive. For this reason the detection limit OFCEAS achieves in the mid-IR region results close to that obtained in the near IR.

A drawback is that the high intracavity laser power combined with the relatively low sample pressure used in order to increase spectral selectivity by absorption line narrowing, may produce saturation effects of molecular transitions, which requires special efforts to be taken into account or minimized.

Quantum Cascade Laser Absorption Spectroscopy (QCLAS) applied for a temperature study of low pressure pulsed dc plasmas

M. Hübner[1], D. Marinov[2], O. Guaitella[2], A. Rousseau[2], J. Röpcke[1]

[1]INP Greifswald, Felix-Hausdorff-Str, 17489 Greifswald , Germany E-mail: huebner@inp-greifswald.de
[2]LPP, Ecole Polytechnique-91128 Palaiseau, France

Quantum cascade laser absorption spectroscopy (QCLAS) has been used to measure the gas temperature during ms dc plasma pulses. The method is based on the intensity ratio of two absorption structures of NO. The influence of non-linear absorption phenomena in the low pressure range was considered by comparison with a simulated spectrum. The reliability of the method was validated at a heated gas cell without plasma ignition.

1. Introduction

Increased concerns about pollution control have led to growing interest in gas cleaning technologies. Plasma technology has proofed its ability to remove harmful gases from an air stream. For these experiments, an important parameter is the gas temperature.

In this contribution, a method is presented which applies quantum cascade laser absorption spectroscopy (QCLAS) to the measurement of the temperature of NO which has been used as a probe gas. This demonstrates the principal possibility to measure the temperature using QCLAS despite the strong disturbance of absorption structures. Such phenomena are caused by non-linear effects, e.g. rapid passage or saturation effects, due to the high tuning rate and intensity of the probing laser.

2. Experimental Setup

The experiments have been done in a tube reactor made of Pyrex with an inner diameter of 20mm and a length of 60cm [1]. QCLAS has been performed using a three channel spectrometer, TRIPLE Q [2], running in the Intra Pulse Mode with a pulse width of 150 ns and a pulse repetition frequency of 30 kHz. For the experiments, the single line absorption structure of NO at 1900.52cm^{-1}, NO($X_{3/2}$, $\upsilon = 0$) → NO($X_{3/2}$, $\upsilon = 1$): R6.5, and the double line absorption structure of NO at 1900.08cm^{-1}, NO($X_{1/2}$, $\upsilon = 0$) → NO($X_{1/2}$, $\upsilon = 1$): R6.5, of a gas mixture of 1% NO in air at 1.3 mbar initial pressure have been used.

The gas temperature has been calculated applying the line ratio method [3]. The ratio of the intensity of two absorption structures depends on the temperature. Consequently, the ratio has been used to study the gas temperature. However, the recorded spectra show huge distortions of the absorption structures due to non-linear absorption effects. These phenomena are not fully understood. There influence, however, has been compensated using simulated spectra with the help of the HITRAN database [4].

From the simulated spectra, a calibration factor has been determined which allows one to calculate the correct temperature from the disturbed spectra.

3. Results

As an example, the temperature at the end of a 5ms dc plasma pulse is given in figure 1. Four mean plasma currents have been applied.

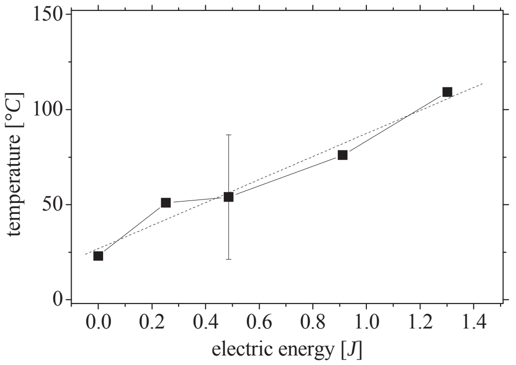

Fig. 1: *Calculated NO temperature of a pulsed dc plasma measured using the line ratio method. The electric energy corresponds to a mean pulse current of 25mA, 50mA, 100mA and 150mA, respectively. The dashed curve shows a linear fit.*

Acknowledgements

This work was supported by the French-German PROCOPE Project D/0502183 and the DFG SFB-TR 24.

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Detection of ozone in an atmospheric pressure plasma jet

J. Winter[1,2], M. Dünnbier[1,2], S. Iseni[1,2], A. Schmidt-Bleker[1,2], K.-D. Weltmann[2], S. Reuter[1,2]

[1]*Centre for Innovation Competence plasmatis, 17489 Greifswald*
[2]*Leibniz Institute for Plasma Science and Technology (INP), Felix-Hausdorff-Str, 17489 Greifswald, Germany*

Ozone detection in the effluent of an atmospheric pressure plasma jet was performed using two different techniques, namely UV absorption spectroscopy in the Hartley band and quantum cascade laser absorption spectroscopy in the mid-infrared spectral region.

1. Introduction

Due to the progress in recent years in the development and research of non-equilibrium atmospheric pressure plasmas with high reactive species densities at low gas temperature, plasma treatment of sensitive surfaces has become possible. Most importantly the possibility of treating living tissue promises frontier breaking therapeutic approaches in the new field of plasma medicine [1, 2]. For a thorough analysis of the interaction of cold plasmas with sensitive biological materials, a detailed quantitative analysis of the reactive component output is required. A prominent reactive molecule that is generated by the plasma is ozone. Since this molecule is biological active and long living it can play a significant role in plasma-cell interaction.

2. Ozone detection methods

In order to determine the ozone density in the effluent of an atmospheric pressure argon plasma jet (kinpen, neoplas GmbH, Germany) with small oxygen admixture (0 - 2%) UV absorption spectroscopy in the Hartley band as well as quantum cascade laser absorption spectroscopy in the mid-infrared spectral region is performed [3]. UV absorption spectroscopy can determine space resolved ozone concentrations, while quantum cascade laser absorption spectroscopy has a high sensitivity and determines the spatially averaged ozone output of the jet with high accuracy, so that even the ozone generation from ambient air oxygen diffusing into the plasma jets effluent at zero oxygen admixture to the feed gas can be quantified.

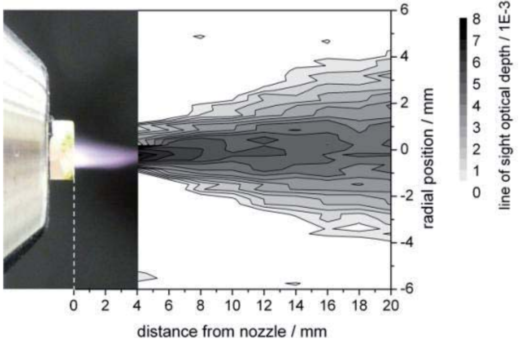

Fig. 1: *Spatial line of sight optical depth of ozone in the vicinity of the jet effluent resulting from the UV-absorption measurement.*

From the UV absorption spectroscopy measurements a two dimensional map of the optical depth of the ozone absorption is recorded (Fig. 1), from which a map of the ozone distribution is calculated via Abel transformation. The IR absorption measurements were performed in a white-cell with an absorption length of up to 16 m. Hence, the density measured with this IR absorption technique does not give space resolved ozone distribution but the averaged density in the cell. However, in order to compare both the ozone detection method in the UV spectral range and the IR absorption measurements the ozone production rate is calculated in both cases. The result is presented in Fig.2. In dependence on the oxygen admixture an increasing ozone production rate was obtained. Furthermore, excellent agreement was found in comparing both ozone detection methods.

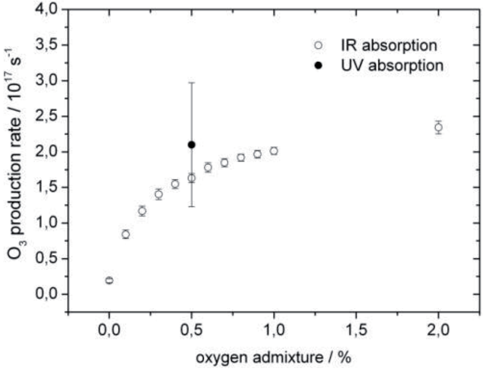

Fig. 1: *Ozone production rate of the investigated plasma jet in dependence on oxygen admixture determined with the IR-absorption technique (open circles) and UV-absorption technique (full circle).*

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In situ and *operando* FT-IR spectroscopy for plasma in catalysis

M. Rivallan, M. El Roz, F. Thibault-Starzyk

Laboratoire Catalyse et Spetrochimie, ENSICAEN, Universite de Caen, CNRS, 6 Bouleavard Maréchal Juin, 14050 Caen cedex

In situ FT-IR spectroscopy was performed in a plasma reactor (low pressure or DBD) for plasma pretreatment of the solid or for plasma-assisted heterogeneous catalysis. Several different reactors will be presented for recording infrared spectra of the gas between the electrodes, together with the spectrum of the solid placed between the electrodes for catalysis or for surface treatment processes. Time resolved spectroscopy allowed kinetic measurements, and some mechanisms of reactions on the solid under plasma were determined.

Recent FTIR spectrometers allow easy measurements on the whole of the mid-IR range at time resolutions up to 5 ns, they can be used to get real time information on plasma treatment of solids or of surface chemistry of solids under plasma.. In the following, a Glow Discharge Reactor was combined with step–scan FT-IR spectroscopy in order to follow excitation mechanisms of CO_2 in air plasma at the microsecond time–scale.[1]

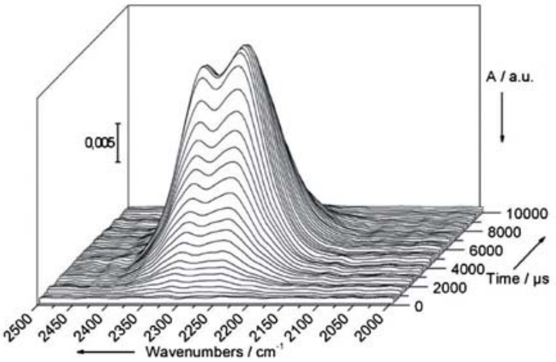

Fig. 1: *IR spectra evolution as a function of time recorded in the discharge zone composed of 15 vol.% CO_2 in air at 10 mbar for 10 ms corresponding to one plasma pulse at t = 0.*

FTIR monitoring of plasma treatment of a solid catalyst was applied to the calcination of metal containing zeolites (Fig. 2) [2,3]. It was particularly helpful in controlling the removal of templates or the conversion of the ammonium form of a zeolite into the acid form at low temperature, without detrimental effect on the morphology of zeolite nanoparticles. The role of water in the plasma was studied.

Catalytic reactions on solids can also be studied with real-time FTIR spectroscopy. The first example studied was isopropanol conversion by DBD on γ-Al_2O_3 catalyst [4]. The role of the solid surface and of the plasma in the reaction was established, and the reaction pathway was established.

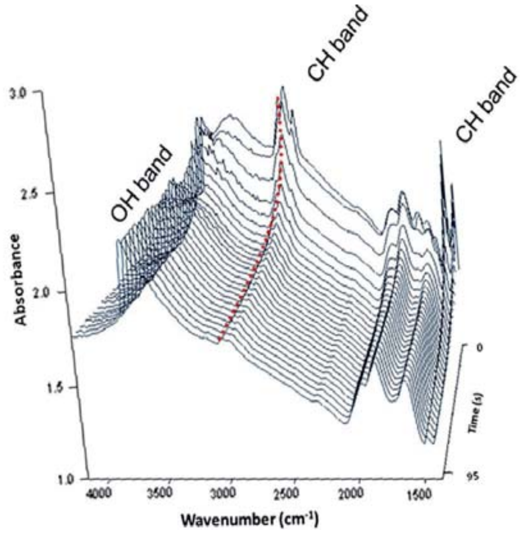

Fig. 2: *Evolution of the mid-IR spectrum of BEA zeolite during the removal of TEA template under oxygen plasma.*

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Plasma Regeneration of TiO_2 Surface Saturated by IPA: Influence of Air Relative Humidity.

S. Loganathan[1, 2, 3], F. Thevenet[1, 2], P. Gravejat[1, 2], A. Rousseau[3].

[1] *Université Lille Nord de France, F-59000, Lille, France.*

[2] *Département Chimie et Environnement, Ecole des Mines de Douai, F-59508, Douai, France.*

[3] *Laboratoire de Physique des Plasmas, Ecole Polytechnique, UPMC, Université Paris Sud 11, CNRS Palaiseau, France.*

Summary

Characterization of gas phase is performed by FTIR spectroscopy down stream a surface discharge ignited on IPA saturated TiO_2. This work aims at (i) Evaluating the regeneration process efficiency, (ii) Understanding the chemistry induced by surface discharge on VOC saturated surface.

Abstract

Indoor air cleaning and volatile organic compound (VOCs) decomposition is becoming most attractive, because air pollution is recognized as a serious issue to humans and living organisms. In the recent years, adsorption of VOCs on metal oxides, and conversion into the useful products or decomposition to CO, CO_2 and water have attracted more attention from the researchers. The regeneration of VOC adsorbed metal oxide surface is challenging task, due to high energy demand and potential deactivation of active sites. In this context, atmospheric pressure Non Thermal Plasma (NTP) is found to be an alternate method, due to its ambient working condition with low energy consumption.

TiO_2 is a widely used metal oxide to adsorb VOCs, and several authors reported that NTP coupled with TiO_2 reactor shows better conversion on gaseous VOCs decomposition comparatively to empty discharge gap reactors [1,2]. Hence, the regeneration of isopropyl alcohol (IPA) saturated TiO_2 surface using NTP surface discharge has been investigated. The NTP assisted TiO_2 surface regeneration was monitored by online FTIR spectroscopy equipped with liquid Nitrogen cooled MCT (Mercury, Cadmium, and Tellurium) detector. Detection limits are: CO_2=10ppb, CO=75ppb, IPA=1.4ppm and Acetone=80ppb.

First, the influence of air relative humidity on IPA adsorption and regeneration has been studied, since moisture is always present in the treated effluents, and H_2O considerably influences the adsorption and oxidation processes [3]. The amount of IPA adsorbed on TiO_2 surface was calculated by breakthrough method using N_2O as tracer. The different modes of IPA adsorption on TiO_2 surface under dry and humid air was investigated. The air relative humidity varied between 0 to 65%, for a fixed flow rate of 1000 sccm. The plasma was ignited with a constant 10 kV AC input voltage, 1000 Hz frequency using homemade high voltage power source. Furthermore, the influence of air humidity (0 to 65%) on plasma injected power has been studied. However, with the fixed applied voltage, the plasma injected power increased from 0.3 W to 2 W due to saturation of TiO_2 surface by water molecules.

Air relative humidity globally decreases the amount of reversible and irreversibly adsorbed IPA on $TiO_{2.}$ However, the regeneration efficiency increased from 35 to 90%. Despite, to achieve 100% carbon balance (complete surface regeneration) TiO_2 surface was heated at 430° C under dry air; thereafter the carbon balance increased to 96%. On the other hand, the most stable side product selectivity Acetone was investigated as a function of air humidity, and found that it decreased from 25 to 3% with increasing air humidity 0 to 65%. In addition to that, the CO_X selectivity as a function of humidity was studied, and it increased from 5 to 25% by increasing air humidity 0 to 65%.

In summary, humid air Non Thermal Plasma Surface discharge treatment efficiently regenerates the IPA saturated TiO_2 surface by oxidizing adsorbed IPA and organic intermediates by using active species such as OH°, O° and O_3 into the close vicinity of TiO_2 surface.

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Plasma-assisted CO_2 reduction in synthetic fuel processing

S. Ponduri[1], S. Welzel[1], F. Brehmer[1], M. Ma[1], M.C.M. van de Sanden[1,2], R.Engeln[1]

[1]*Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands E-mail: s.welzel@tue.nl*
[2] *Dutch Inst. for Fundam. Energy Research (DIFFER), P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands*

Infrared laser absorption spectroscopy (IR-LAS) in conjunction with mass spectrometry was used to characterize the CO_2 reduction in expanding Ar/H_2 plasmas for synthetic fuel production. CO_x was injected into the expansion part where the reaction mechanism could be radical and/or ion driven. The results suggest a separation of dissociation and hydrogenation step. Further work on materials tailored for plasma-catalysis is required to increase the conversion efficiency.

1. Introduction

Plasma processing of carbon dioxide into conventional fuels is considered as an alternative approach. While reducing the green house gas emissions, these fuels can be integrated in the existing transport infrastructure. The formation of CO from CO_2 is thereby considered the rate limiting step [1] in further hydrocarbon or oxygenate forming reactions. This paper discusses conversion efficiencies in plasma-assisted CO_2 reduction, i.e. dissociation and hydrogenation in a low temperature plasma expansion. The potential of plasma catalysis in this context is assessed.

2. Experimental

CO_2 was injected into the background of an expanding thermal plasma created from a cascaded arc in mixtures of H_2 and Ar. The flow of CO_2 was maintained at about 10% of the total flows of 3360 sccm. The total pressure in the magnetized expansion part, where the electron temperature is usually clearly below 1 eV, was kept at 1 mbar.

The plasma composition was characterized at the farther end of the plasma expansion using infrared laser absorption spectroscopy (IR-LAS). Quadrupole mass spectrometry (QMS) was used as a complimentary technique for measuring components that cannot be accessed by IR-LAS. Apart from the native stainless steel, aluminium and copper foils were used in close contact to the vacuum vessel to evaluate the influence on the steady-state gas composition.

3. Results and Discussion

Three distinct regimes of chemistry can be observed depending on the gas composition through the arc (from pure Ar to pure H_2, fig. 1). In the first regime (I) charge exchange between CO_2 and Ar^+ ions followed by dissociative recombination of CO_2^+ - as observed for other molecular gases in this type of plasma - may be the dominant process. Ar^+ is quenched quickly with addition of few percentage of H_2 to the flow [2] and so are the O_2 production and the CO yield which can be as high as 50 % in pure Ar.

In regime II the CO_2 dissociation levels off and production of methane starts (fig 1). Main stable products apart from CO_2 are CO and H_2O (not shown in fig. 1). In regime III the chemistry is mainly driven by H radicals which leads to an increase in methane production. However, the CH_4 remains at a few %.

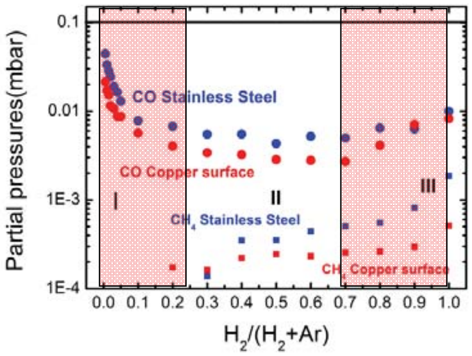

Fig. 1: *CO and CH_4 produced during the CO_2 reduction in a plasma expansion of Ar/H_2 using different surface materials. Different regimes of chemistry are indicated (I - III).*

Experiments performed with CO in place of CO_2 - where the conversion to methane starts at much lower additions of H_2 and may reach 25 % - confirmed that a syngas step ($CO+H_2$) is also essential in plasma-catalytic approaches. A difference in the gas composition was observed, when certain surface materials were used (e.g. Cu, fig. 1). However, in contrast to conventional catalysis the CO concentration was reduced and so was the CH_4 formation.

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SESSION 5

Wednesday 16th, 9h00

Probing combustion and other harsh environments using laser spectroscopic techniques

Marcus Aldén

Division of Combustion Physics, Lund University, P.O. Box 118, S-221 00 Lund, Sweden

Examples will be given from a variety of laser techniques, where high speed visualization, multi-species visualization and ways to detect “new” species will be highlighted both from a more fundamental perspective but also with several “real-world” applications.

Introduction

The importance of combustion processes for efficient and environmentally friendly energy conversion, e.g. for heat production and for transportation have encouraged research on new tools for a deepened understanding of these processes. During the last decades different laser diagnostic techniques have proven to be very valuable tools for measurements in harsh environments, e.g. different combustion situations. The main advantages with these techniques are the non-intrusiveness in combination with high spatial and spectral resolution. Parameters that can be measured are species concentrations (atoms, molecules, radicals), temperatures (vibrational, rotational, translational and electron), velocities and characteristics of particles (size, number density, volume fraction) and surfaces. The techniques that have been used can be divided into non-coherent and coherent techniques, where the former include, e.g. Mie, Rayleigh and Raman scattering, laser-induced fluorescence, whereas the latter include e.g. Coherent anti-Stokes Raman Scattering (CARS), polarization spectroscopy (PS), degenerate four-wave mixing (DFWM) and Stimulated emission (SE). See Refs. [1,2] for some overview articles.

Non-coherent techniques

Maybe the most important technique for diagnostics is laser-induced fluorescence, LIF, with which two-dimensional measurements can be made. It has also been shown that high speed, ~10-100 kHz, can be realized. In Fig 1 is shown high speed visualization of OH in a turbulent flame

Coherent techniques

As an alternative technique there are also Coherent techniques where the signal is generated as a new laser beam. An example is given in Fig. 2. Here H atoms are measured in 2D in a flame using polarization spectroscopy.

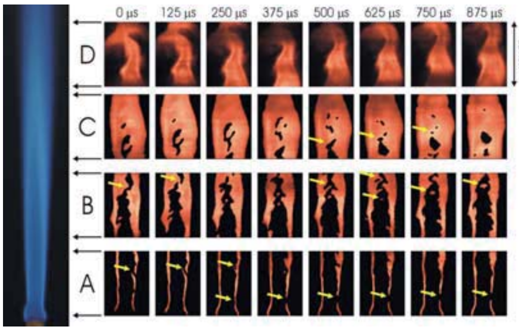

Fig. 1 *High speed visualization of OH radicals at different heights in a turbulent flame using laser-induced fluorescence*

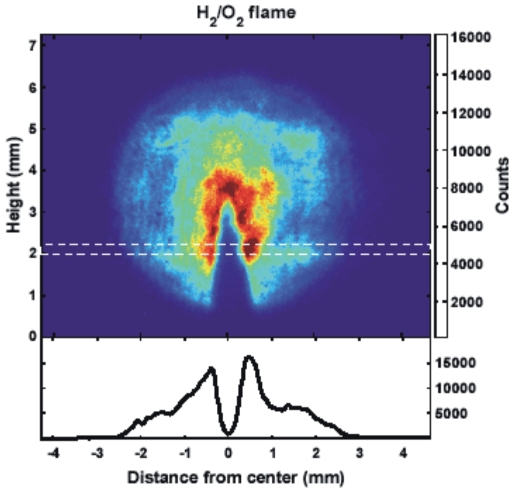

Fig 2. *Single shot distribution of hydrogen atoms in a flame measured with polarization spectroscopy*

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Chlorine atom and molecule dynamics in an inductively coupled plasma in pure Cl_2

J.P. Booth, P. Chabert, Y. Azamoum and N. Sirse

LPP-CNRS, Ecole Polytechnique-91128 Palaiseau, France E-mail: jean-paul.booth@lpp.polytechnique.fr

Two-photon laser-induced fluorescence (TALIF) was used to measure the absolute densities of Cl atoms and Cl_2 molecules with high spatial and temporal resolution in an inductively-coupled plasma in pure Cl_2 for pressures ranging from 2 to 50 mTorr and RF power (13.56 MHz) of 20 to 500W. The TALIF method of Ono et al. was used to detect the atoms, but a new scheme was developed to put the densities on an absolute scale, using 355nm laser photolysis of Cl_2 gas to produce a well determined density of Cl atoms. Firing the photolysis laser during plasma operation produces an increase in the TALIF signal proportional to the (local) Cl_2 density, allowing this quantity to be measured. In this way the total gas density (nCl + nCl2) was determined, and found to me considerably below the gas density without plasma, indicating that the gas is heated to high temperatures in the plasma.TALIF was also used to monitor the decay of the Cl atoms in the afterglow of a pulsed plasma, allowing the Cl surface recombination on Al_2O_3 to be studied.

1. Introduction

Two-photon laser-induced fluorescence (TALIF) is a powerful technique to measure relative atom densities with high spatial and temporal resolution. Niemi et al. [1] proposed a scheme for putting TALIF measurements of H, O and N atoms on an absolute scale by comparing the signal to that generated from a known density of a rare gas (Kr or Xe). Unfortunately in the case of Cl there is no TALIF transition in any rare gas at a close wavelength, so a such a scheme cannot be used. We have developed an alternative technique based on photolysis of a known density of Cl_2 molecules at 355nm. The Cl_2 absorption cross-section at this wavelength is known with high precision ($15.9 \times 10^{-24} m^2$), and photon absorption leads to dissociation of the Cl_2 molecule with 100% yield, producing two Cl atoms with a velocity of $1700 ms^{-1}$. Using an unfocussed tripled Nd:YAG laser for the photolysis provides a well characterised photolysis beam with a diameter much greater than that of the TALIF laser focus, so that the Cl_2 dissociation fraction can be calculated with high precision. In addition Cl_2 molecule densities were determined by measuring the additional TALIF signal created when the 355nm laser is fired during plasma operation. Finally, decays of the Cl density in the afterglow were measured by firing the TALIF laser at variable delays into the afterglow of a pulsed plasma.

2. Experimental

The plasma was produced in a cylindrical chamber (hard anodised Al, 10cm high, diameter 55 cm) excited by an external planar spiral coil at 13.56 MHz through an alumina window. Cl atoms were excited by two photons at 233.2 nm (supplied by a pulsed Nd:YAG pumped dye laser with frequency doubling) focussed at the reactor centre, and detected by 726 nm fluorescence as described by Ono et al.[2]. For the calibration, the reactor was filled with Cl_2 gas at room temperature (without plasma). The counter-propagating 355nm photolysis beam overlaps the TALIF beam at the reactor centre. We calculate that at the photolysis beam centre the photolysis yield is 6.7%, so that the Cl atom density created is 13.4% of the pre-laser Cl_2 molecule density).

3. Results and discussion

Fig 3 shows the Cl density as a fraction of the Cl_2 density (before plasma). This fraction first increases with power, then saturates. The highest fraction is observed at the lowest pressure, reaching 20% at 50mTorr 500W. Increased RF power causes faster electron-impact dissociation of Cl_2, but also causes significant gas heating, lowering the total gas density at constant pressure, which is the principal cause of the saturation well below 100%.

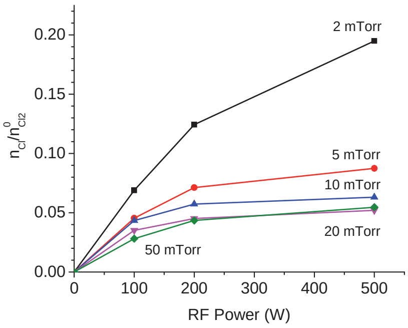

Fig 1. Cl TALIF signals from the plasma and from laser photolysis

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InP Based QCL for spectroscopy at III-V Lab

M.Carras[1], G. Maisons[1], B. Simozrag[1]

[1] *III-V Lab, Ecole Polytechnique-91128 Palaiseau, France E-mail: mathieu.carras@3-5lab.fr*

We show the development at III-V lab on QCLs for spectroscopy applications. After explaining the specific approach on metal grating DFB, we present the future development on integrated sources

QCLs are the main semiconductor source for easy to use continuous wave operation in the MIR. The MIR is particularly interesting for the spectroscopy because it presents several windows of atmospheric transmission (with rare and weak absorption lines of H2O and CO2) where we find fundamental ro-vibrational absorption lines of several atmospheric pollutants (NO, N2O, CO, H2CO (formaldehyde) NH3, SO2, etc). These fundamental bands are 2 to 3 orders of magnitude more intense than their harmonics in the near infra-red range (1.0-2.5 µm). Moreover, the majority of the complex organic molecules (more than 5 atoms) which have an interest for defense and safety have also their signatures between 7 and 12 µm.

As for NIR diode, QCL present the possibility of fabricating distributed feedback lasers by using intra-cavity grating for the wavelength selection. There are two main ways of fabricating such device, by buried grating or surface metal gratings. The first is more conventional and is the first one to have led to continuous wave laser [1]. The second is far more easy to use and show similar performances. We have developed such laser at III-V Lab with continuous wave operation at room temperature [2] for the detection of formaldehyde in the framework of ANR project ApolinR []as shown in fig. 1.

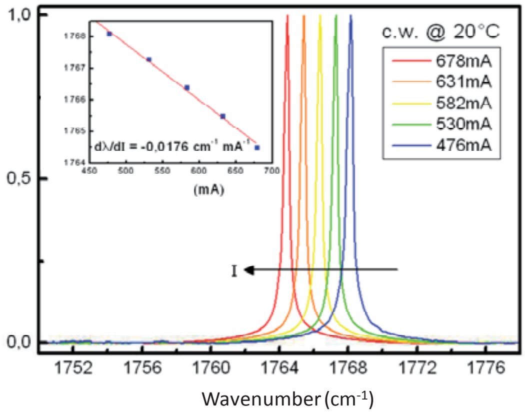

Figure 1 : Example of DFB laser spectra for formaldehyde

These sources enable fine tuning of the laser wavelength (typically a few cm^{-1}). This is sufficient for simple molecules (ie. a few atoms as shown on Fig. 4 with atomic labels) but not for multi-gas applications or complex molecule detection. That is why, in recent developments, widely tunable sources start to be developed.

There are again two ways of obtaining those sources, either by external cavity wavelength and grating or by fabrication of laser arrays.

External cavities based on QCLs are already developed as products [4]. Those products have the advantage of being the first to propose wide tenability. However, they still suffer from complexity, stability, high price.

Another solution consists in DFB arrays. The principle is to fabricate series of N laser, each lasers being at a central wavelength at a few cm^{-1} from its neighbors. Fig 5 shows the result of such a device. Be switching on one after the other each QCL, we obtain a tunable source [5]. The main problem is the use of the output of the laser. A solution is the use of integration.

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The Use of Optical Emission Spectroscopy for Inline Monitoring of the Atmospheric Pressure Plasma Pre-treatment Process in Adhesive Bonding Technology

H. Hildebrandt, S. Stepanov, S. Markus, J. Ihde, U. Lommatzsch, S. Dieckhoff

Fraunhofer Institute for Manufacturing Technology and Advanced Materials (Fraunhofer IFAM)
Wiener Strasse 12, 28359 Bremen, Germany. E-mail: sergey.stepanov@ifam.fraunhofer.de

1. Introduction and motivation

An appropriate state of adherend surfaces is essential for stability and reliability of an adhesive bond. Therefore, an effective surface cleaning and/or activation are a key issue for the adhesive bonding technology. Atmospheric pressure plasma jets are often used for pre-treatment in industry, due to their high compatibility with existing process chains. However, efficiency of the pre-treatment regarding the quality of the adhesive bond can often be evaluated only by destructive mechanical tests. Therefore, methods to analyse the surface state and the plasma processing before the bonding are sought for a quality assured pre-treatment.

Laser Induced Breakdown Spectroscopy (LIBS) is a type of optical emission spectroscopy (OES) which enables detection and semi-quantitative analysis of characteristic contamination species on the sample surface excited by means of a laser. In particular, intensity ratios of the detected emission lines measured before and after the plasma processing can provide information on efficiency of the pre-treatment process. In the present work, a similar approach was developed, whereas the plasma jet applied for the surface pre-treatment was simultaneously used as an excitation source for an oil-like contamination on the treated substrates. Thus, plasma pre-treatment and process control were combined. The LIBS technique was also employed in this study as a reference method.

2. Experimental part

Aluminium substrates contaminated with a lubricant commonly used for the sheet metal forming were chosen as a model system in the following studies. Defined amounts of the lubricant were sprayed on the substrates resulting in various contamination concentrations up to 5 g/m^2. An atmospheric pressure plasma jet operated with compressed air was applied for the surface treatment of the substrates, whereas the plasma jet served simultaneously as an excitation source for the lubricant components measured by OES. Emission of the excited species was collimated, focused into an optical fiber and analysed in the spectral range from 200 nm to 800 nm using two spectrometers of different spectral resolution.

3. Results

Sodium and calcium were found to be characteristic elements in the selected contamination. These elements are well detectable during the plasma treatment by means of OES (Fig. 1). Aluminium emission lines from the substrate were used as reference signal. Ratios of the peak areas from calcium and aluminium could be assigned to different amounts of the lubricant on the substrates (Fig. 2). This provided a tool to analyse the surface state of the treated samples and thus monitor the efficiency of the plasma treatment during the process. Finally, the obtained results were verified by LIBS measurements.

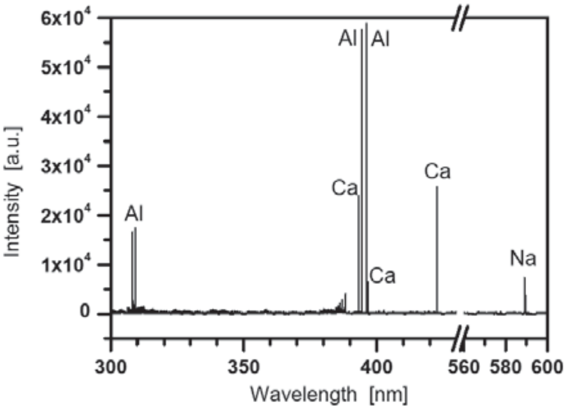

Fig. 1: *Typical emission spectra measured during the plasma treatment of contaminated Al-substrate.*

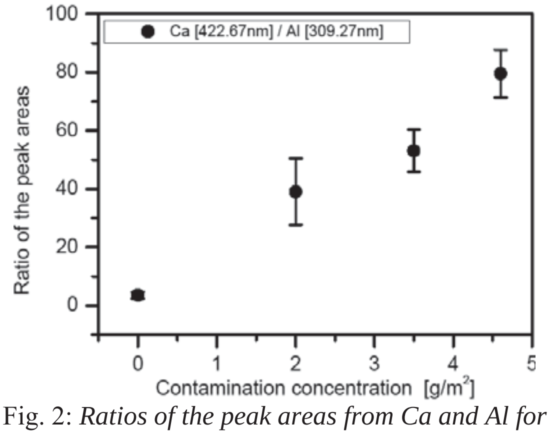

Fig. 2: *Ratios of the peak areas from Ca and Al for different amounts of lubricant on the plasma treated Al-substrates.*

Particle Characterization by means of White Light Scattering

S. Mitic[1] , M. Y. Pustylnik[1] , G. E. Morfill[1] , E. Kovačević[2]

[1] *Max-Planck-Institut für Extraterrestrische Physik, Garching,, Germany E-mail: mitic@mpe.mpg.de*
[2] *GREMI, Orleans University, Orleans Cedex 2, France*

In this paper recant development in characterization of spherical nanoperticles with monotonically variable size suspended in plasma is reported. Method is based on solving the reversed problem of light scattering from spherical particles which radius is monotonically changing in time e.g. particle growth or etch in plasma. The measurements are in-situ and nonintrusive requiring three optical exes: one for illumination of particle cloud by white light and two for measurement of the spectra of the scattered light. As a result the wavelength dependent refractive index of particle suspension is reconstructed together with time dependent radius.

1. Experiment

Many different experimental methods were reported for diagnostic of spherical particles suspended in plasma. However most of them require moving parts, multiple optical axes, complicated optics or long measurement. Method presented here overcomes all these problems and leaves space for more improvements.

The experiments are done in PK−4 setup [1], which is laboratory prototype of parabolic flight and future International-Space-Station-based complex plasma facility. The hart of the setup is long cylindrical 30 mm diameter glass tube. Plasma is generated by 81 MHz RF current driven through the loop of wire around the tube.

Two types of experiments were done. First, scattered light from particles grown on argon acetylene mixture were measured [2]. Second, PS particles with known size were etched in Argon oxygen plasma and light evolution were recorded. Assuming that the refractive index of the particles is not time dependent and not varying with size, the evolution of light signal for one wavelength scattered form particles could be reconstructed into the time dependent radius r(t) fitting the refractive indexes for the rest of the illumination spectra using r(t) as time dependent radius. This procedure is repeated until minimal error between reconstructed light intensity evolution and measurement is reached. For light scattering simulation mie theory is used [3].

2.Results

Figure 1. up shows the reconstructed indexes of grown particles for different starting wavelength, blue 725nm, red 746nm and green 781nm. Full lines shows real part on the right y axis while lines with symbols shows imaginary part on the left y axis. Black line, full and with symbols represents refractive index of the 1.3 μm diameter PS particle etched in argon oxygen plasma. In the lower figure respective time dependent radii are shown.

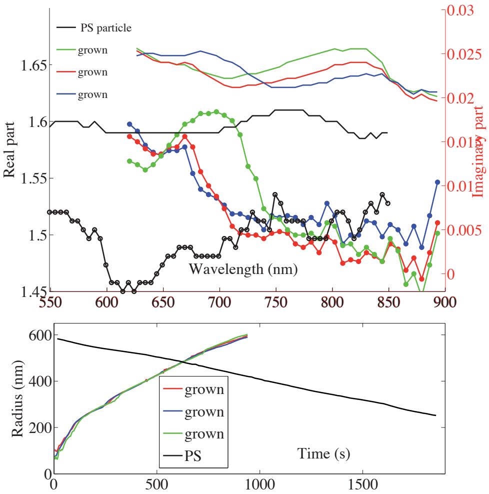

Fig. 1: *Wavelength dependent refractive indexes of grown and PS particles together with their time dependent radii.*

References

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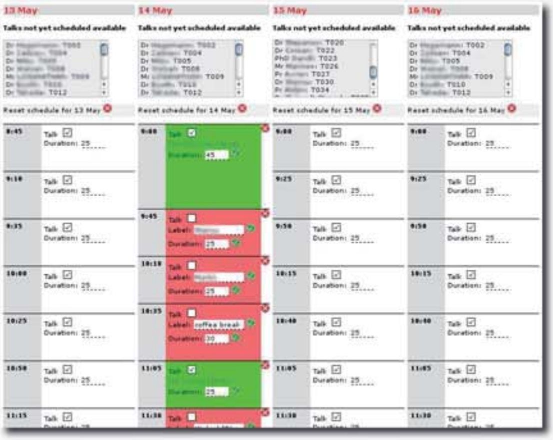

13 May	14 May	15 May	16 May
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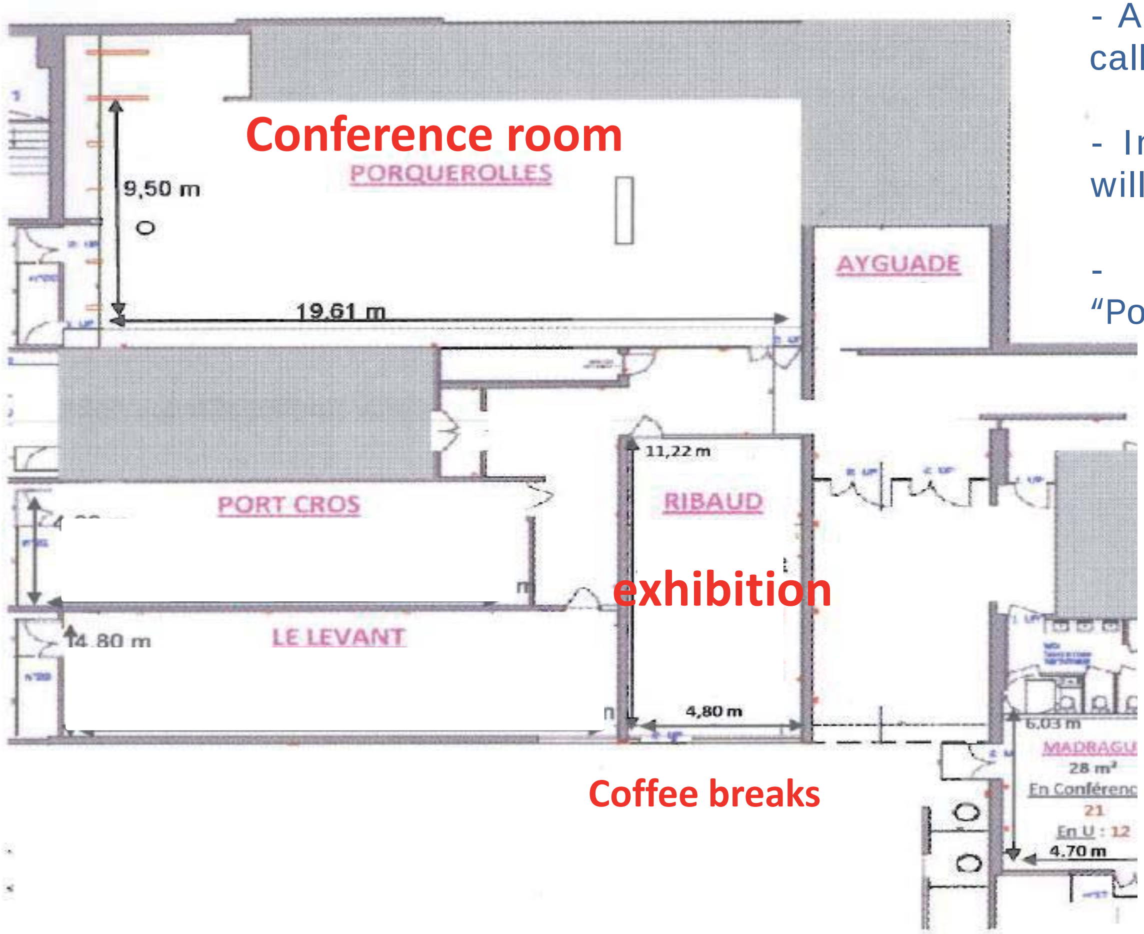

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Pr Ove Axner	Umea University	ove.axner@physics.umu.se	Sweden
Dr Grant Ritchie	University of Oxford	grant.ritchie@chem.ox.ac.uk	UK
Dr Daniele Romanini	University J. Fourier-Grenoble	daniel.romanini@ujf-grenoble.fr	France
other participants			
Dr Viacheslav Artyushenko	art photonics GmbH	sa@artphotonics.com	Germany
Mr Retail Bertrand	Hiden Analytical Limited	b.retail@hiden.fr	ENGLAND
Dr Jean-Paul Booth	LPP-CNRS	jean-paul.booth@lpp.polytechnique.fr	France
Mr guillaume Bourgeois	ICARE CNRS	guillaume.bourgeois@cnrs-orleans.fr	France
Dr Antonin Brablec	Masaryk University	abr92@elanor.sci.muni.cz	Czech Republic
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Mr Grégory Candor	Bruker	gregory.candor@brukeroptics.fr	France
Dr Mathieu Carras	III-VLab	mathieu.carras@3-5lab.fr	France
Mr Rafal Chodun	Faculty of Materials Science and Engineering, Warsaw	rchodun@op.pl	Poland
Dr Mihaela Cirisan	Laboratoire LP3, CNRS - Université Aix-Marseille	cirisan@lp3.univ-mrs.fr	France
Mr Stéphane Crochetet	ENTREPRISE LECROY	stephane.crochetet@lecroy.com	FRANCE
PhD Thomas Dandl	Technical University of Munich, Physics Department E12	thomas.dandl@tum.de	Germany
Pr Paul Davies	University of Cambridge	pbd2@cam.ac.uk	United Kingdom
Dr Eugenio Fasci	CNRS/LPP	eugenio.fasci@lpp.polytechnique.fr	FRANCe
Mr Fresquet William	Andor Technology	W.Fresquet@andor.com	UK
Dr Zanda Gavare	Institute of Atomic Physics and Spectroscopy, University of Latvia	zanda.gavare@gmail.com	Latvia
Dr Paul Gravejat	Ecole des mines de Douai - Departement Chimie et Environnement	paul.gravejat@mines-douai.fr	France
Dr Dirk Hegemann	Empa	dirk.hegemann@empa.ch	Switzerland
Dr Frank Hempel	INP Greifswald	hempel@inp-greifswald.de	Germany
Mr Bartosz Hrycak	The Szewalski Institute of Fluid-Flow Machinery PAS	bhrycak@imp.gda.pl	Poland
PhD Huebner Marko	INP Greifswald	huebner@inp-greifswald.de	Germany
Dr Norbert Lang	INP Greifswald	lang@inp-greifswald.de	Germany
Mr Arnaud Langlois	OPTOPRIM	alanglois@optoprim.com	France
Mr Sivachandiran Loganathan	Ecole des mines de douai	loganathan.sivachandiran@mines-douai.fr	France
Mr Dmitry Lopatik	INP Greifswald	lopatik@inp-greifswald.de	Germany
Mr Daniil Marinov	CNRS/LPP	daniil.marinov@lpp.polytechnique.fr	France
Dr Philip Martin	University of Manchester	philip.martin@manchester.ac.uk	UK
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Pr Rainer Martini	Stevens Institute of Technology	rmartini@stevens.edu	USA
Dr Vera Mazankova	Brno University of Technology	mazankova@fch.vutbr.cz	Czech Republic
Dr Slobodan Mitic	Max Planck Institute for Extraterrestral Physics	mitic@mpe.mpg.de	Germany
Mr Stefan Muthmann	IEK-5 Photovoltaik, Forschungszentrum Juelich	s.muthmann@fz-juelich.de	Germany
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LOC:			
Dr Antoine Rousseau	LPP/CNRS	antoine.rousseau@lpp.polytechnique.fr	France
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IPS 2012 Workshop Schedule

	Sunday	Monday	Tuesday	Wednesdday
8:30				
8:45		Registration		
9:00		opening		
9:15		G. Ritchie	O. Axner	M. Alden
9:30				
9:45				
10:00		D. Marinov	A.F.H. van Gessel	J.P. Booth
10:15		P.A. Martin	K.Takeda	M. Carras
10:30				
10:45		coffee break (30 min)	coffee break (30 min)	coffee break (30 min)
11:00				
11:15		N. Lang	I. Marinov	S. Stepanov
11:30				
11:45		G. Stancu	D. Hegemann	S. Mitic
12:00		S. Welzel	M. Cirisan	
12:15				
12:30		lunch break (60 min)	lunch break (60 min)	lunch break (60 min)
12:45				
13:00				
13:15				
13:30		free discussions	free discussions	
13:45				
14:00				
14:15				
14:30				
14:45				
15:00				
15:15				
15:30				
15:45				
16:00				
16:15		R. Martini	D. Romanini	
16:30				
16:45		V.I. Zaitsev		
17:00		T. Dandl	M. Hübner	
17:15			J. Winter	
17:30		coffee break and Poster session and Industrial exhibition		
17:45	Registration		coffee break (30 min)	
18:00				
18:15			Thibault-Starzyk	
18:30				
18:45	Welcome drink		S. Loganathan	
19:00			S. Ponduri	
19:15				
19:30				
19:45	diner	diner	conference diner	
20:00				
20:15				
20:30				
20:45				
21:00				
21:15				
21:30				