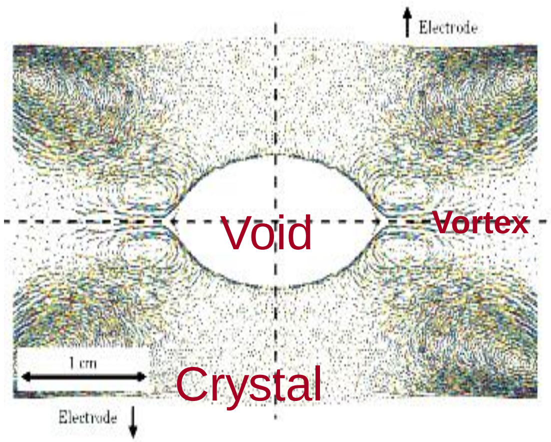
Плазма з нано- та мікрочастинками та взаємодія плазмових потоків з поверхнями твердих тіл

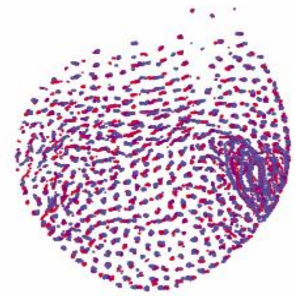
- *У кінетичному наближенні буде вивчено фізичні процеси у молекулярній лабораторній плазмі з нано- та мікрочастинками; процеси, що відбуваються у нестаціонарній запорошеній плазмі; та процеси, що відбуваються за електричного пробою у суміші газів, що відповідає атмосфері Марсу.*
- *Також буде досліджено взаємодію плазмових потоків з поверхнею твердого тіла; експериментально виявлено особливості люмінесценції при опроміненні кварцу іонізуючим випромінюванням та іонами різних типів і енергій; визначено вплив дифузії імплантованих частинок на зміни в спектрах люмінесценценції.*

Contents

From microgravity experiment:



G. E. Morfill et al.
Phys. Rev. Lett. **83**, 313 (1999).



Dust ball

O. Arp, D. Block, A. Piel, A.Melzer
Phys. Rev. Lett. ***93**, 165004 (2004).*

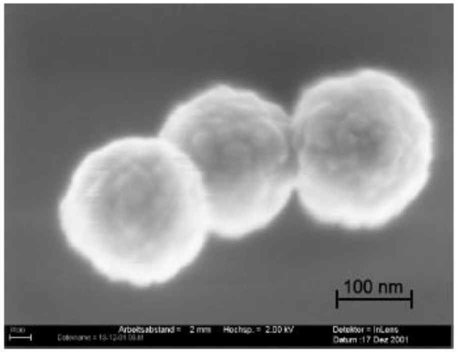


FIG. 7. SEM micrograph of particles collected 10 min after plasma ignition.

Formation of dust particles in a glow capacitively coupled discharge: a_d = 10-275 nm, $n_d \sim 10^7$ cm^{-3}, Ar + C_2H_2 (SiH_4).

J. Berndt et al, Plasma Sources Sci. Technol. ***15,** 18 (2006).*
M. Hinz, E. von Wahl, F. Faupel, T. Strunskus, H. Kersten,
J. Phys. D: Appl. Phys. ***48**, 055203 (2015).*

•Complex (dusty) plasma is interesting from fundamental point of view (formation of different structures, interaction between particles).
•Dust particles can be introduced into a plasma volume from outside or be formed due to different chemical reactions and interaction of plasma fluxes with the walls.
•Complex plasma is also interesting for many technologies.

•*H. Kersten et al. Contrib. Plasma Phys.* ***41**, 598 (2001). L Boufendi, MC Jouanny, E Kovacevic, J Berndt, M Mikikian, J. Phys. D: Appl. Phys.* ***44**, 174035 (2011).*

- Formation of carbonaceous dust particles takes place in gas discharges containing methane, acetylene or ethylene.

- Measurements in Ar/C_2H_2 plasmas showed that formation of dust particles is accompanied by a decrease of acetylene and electron densities and by an enhancement of T_e and density of metastable argon atoms.

[Herrendorf A P, Sushkov V and Hippler R 2017 J. Appl. Phys. ***121*** *123303*
Berndt J, Kovacevic E, Stefanovic I and Boufendi L2009 J. Appl. Phys. ***106*** *063309*
Winter J, Berndt J, Hong S H, Kovačević E, Stefanović I and Stepanović O 2009 Plasma Sources Sci. Technol. ***18****034010].*

- The degree of C_2H_2 dissociation in an Ar/C_2H_2 plasma at formation of nanoparticles can be as high as 99%. The densities of electrons and metastable argon atoms were simultaneously measured in the glow and afterglow regimes of a pulsed RF Ar/C_2H_2 plasma for the dust-free and dusty plasma cases.

Stefanović I, Sadeghi N, Winter J and Sikimić B 2017 Plasma Sources Sci. Technol. ***26*** *065014*

- Properties of C_2H_2 and Ar/C_2H_2 RF plasmas were also studied by computer simulations allowing to explain the nucleation of nanoparticles in these chemistries. In particular, it was shown that both positive and negative ions may participate as precursors in the initial stage of particle formation.

Stoykov S, Eggs C and Kortshagen U 2001 J. Phys. D: Appl. Phys. ***34*** *2160*
De Bleecker K, Bogaerts A and Goedheer W 2006 Phys. Rev. E ***73*** *026406*
Mao M, Benedikt J, Consoli A and Bogaerts A 2008 J. Phys. D: Appl. Phys. ***41*** *225201*
Schweigert I V, Alexandrov A L and Ariskin D A 2014 Plasma Chem. Plasma Process. ***34*** *671*

- Most of these numerical studies considered only the initial stages of particle formation and, therefore, they did not account for effects of dust particles on plasma properties, which may be essential in some experiments.
The time-dependencies for densities of ions and neutral species and the effects of dust particles in the afterglow of Ar/C_2H_2 plasmas have not been studied yet.

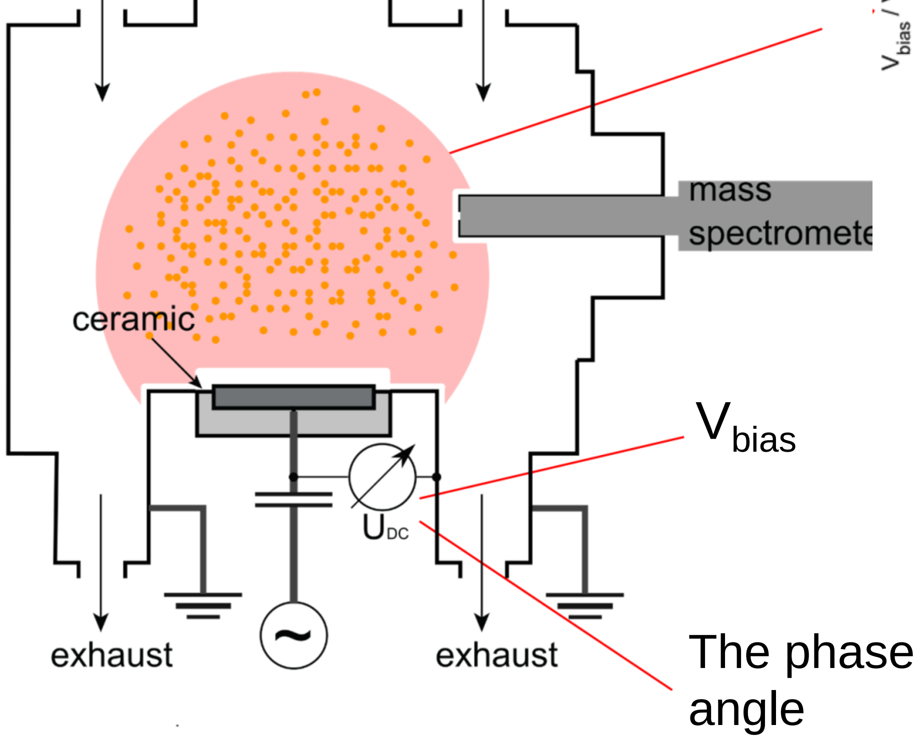
- We analyse the properties of an Ar/C_2H_2 dusty plasma (ion, electron and neutral particle densities, T_e and Z_d) in the glow and afterglow regimes using a global (volume-averaged) model.

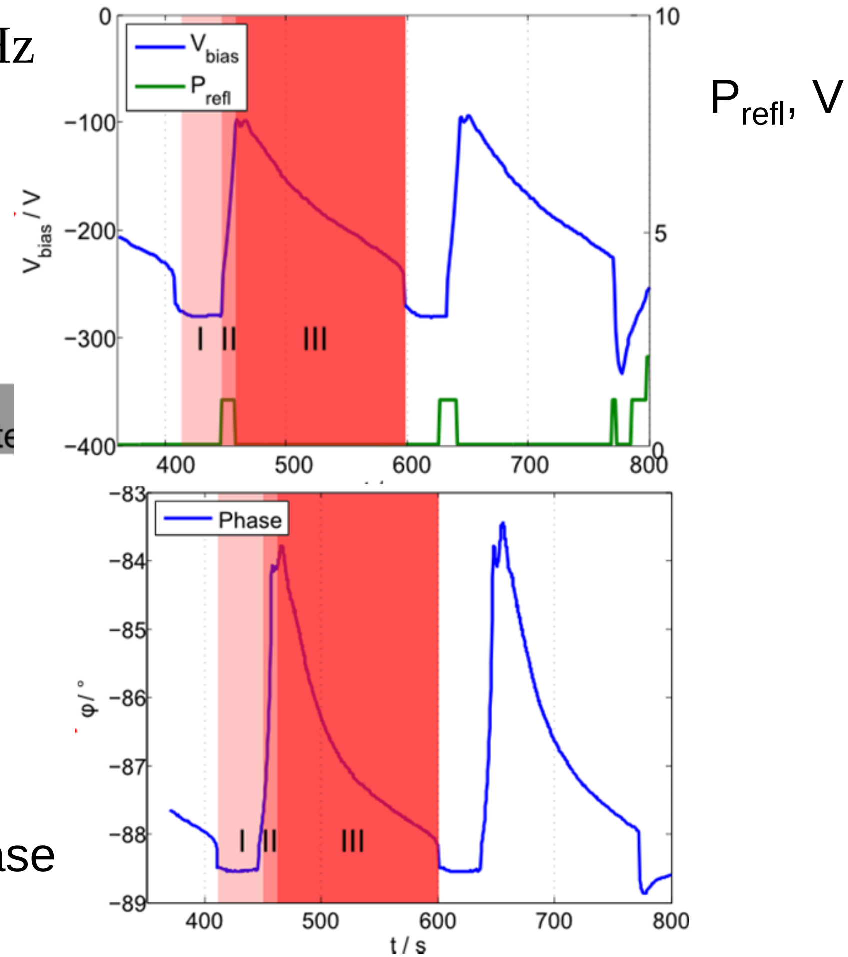
- The effect of dust particles on the steady-state gas-discharge properties is studied, and the properties of dust-free and dusty-plasma afterglows are compared.
A comparison with experimental data is carried out.

Experiment

L ≈32.4 cm, *R*≈22 cm
Q_{C2H2}=1.11 sccm,
Q_{Ar}=10.1 sccm

f =13.56 MHz
P_{in}= 9 W
$P \approx 5$ Pa





After plasma ignition and under particular plasma conditions, the discharge displays a periodic behaviour.

Time evolution of the self-bias voltage and the phase angle between the RF current and voltage.

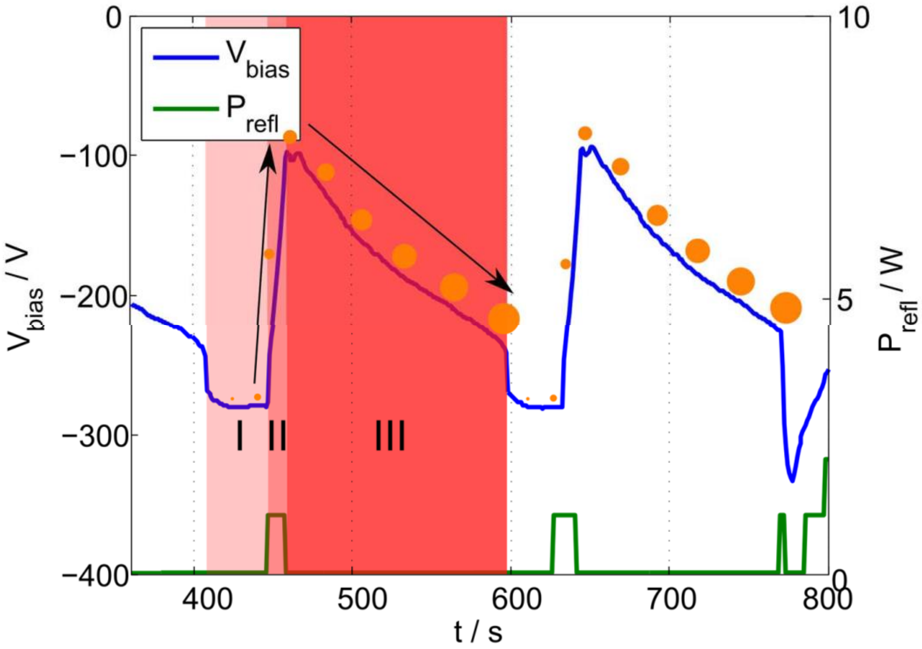
Performing *ex situ* SEM measurements, we determined the nanoparticle size in different growth phases. Dust radius was growing with time during a cycle.

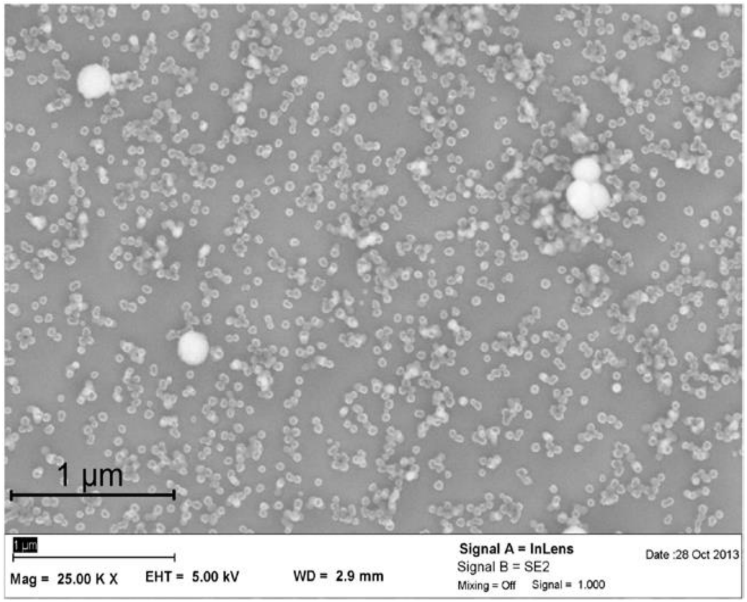
The measurable nanoparticle diameter

Phase I: 20-40 nm (do not modify plasma properties)

Phase II: 40-50 nm

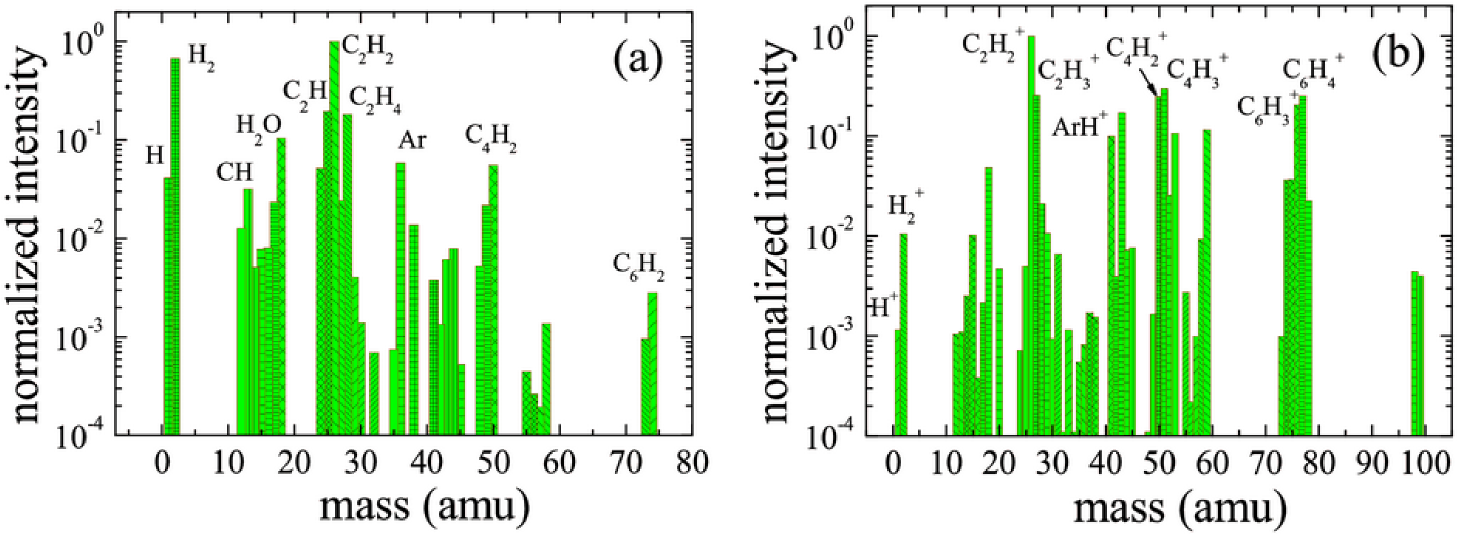
Phase III: 50-140 nm (dust particles leave the discharge at the phase end)





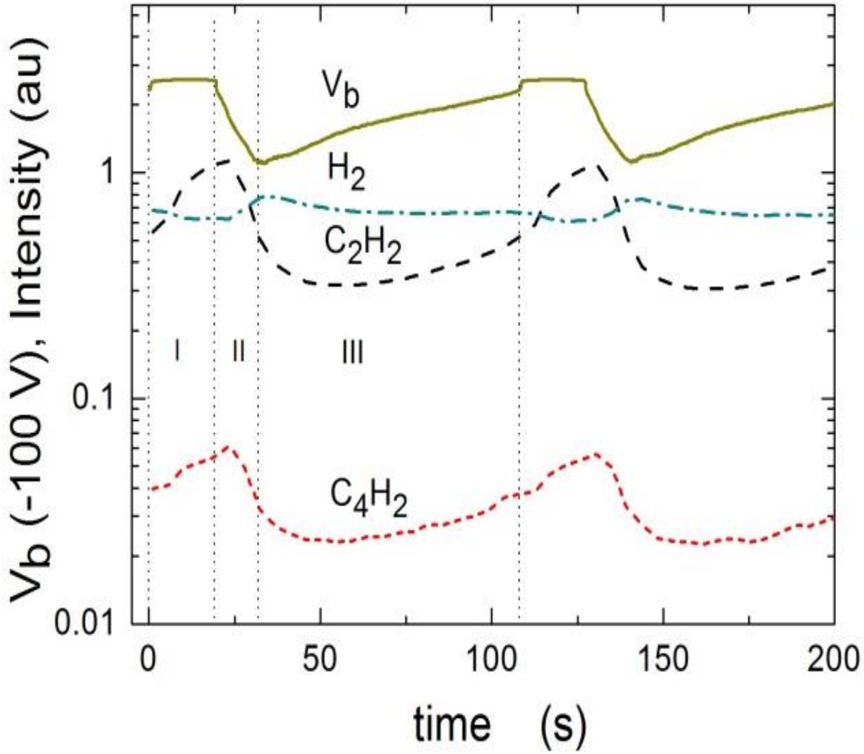
[A. M. Hinz *et. al.*, J. Phys. D: Appl. Phys. **48** 0555203 (2015)].

The mass spectra measured using the Hiden PSM 003 mass spectrometer at a height of 10 cm and a radial distance of 7 cm from the center of the powered electrode (Phase I).



- C_2H_2 and H_2 are the dominant molecules, C_2H_4, H_2O and C_4H_2 are also important. The peak at 28 amu may be due to an input of C_2H_4 and N_2 in the discharge chamber. The radicals (H, C_2H, etc.) may be due to processes in the spectrometer chamber.
- The significant ion species in the plasma are $C_2H_2^+$, $C_2H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_6H_4^+$ and $C_6H_3^+$.

We did not measure the intensities of Ar+ and Ar (40 amu) simultaneously with other species (the intensity was much above saturation, the instrument would shut down).



The self-bias voltage V_b and the mass peaks of C_2H_2, H_2, C_4H_2 during a growth cycle. t = 0 corresponds to 2435 s from the plasma ignition.

- The peaks of C_2H_2 and C_4H_2 decrease during the 2-nd half of phase II and the first half of the phase III (probably, before void formation).

- The peak of H_2 is decreasing in the phase III.

- The peak of H_2 is larger than that of C_2H_2 in the phase III.

- The phase I has to be considered carefully as it follows phase III of the previous cycle and could be impacted by previous dust generation.

The volume-averaged (0D) model of Ar/C_2H_2 dusty plasma

4 nonradical neutrals	2 radicals	Ar atoms in excited states	9 positive ions	Negatively charged particles
Ar, C_2H_2, H_2, C_4H_2	C_2H, H	Metastable ($^3P_0$ and $^3P_2$) and resonance ($^3P_1$ and $^1P_1$) 4s states and 4p states	$C_2H_2^+$, Ar^+, ArH^+, H_2^+, H^+, $C_4H_3^+$, $C_4H_2^+$, $C_6H_4^+$ and $C_2H_3^+$	electrons, anions C_2H^-, dust particles: $n_d \sim 10^7$ cm^{-3}, $a_d \sim$ 10-70 nm

L =32.4 cm, *R* = 22 cm, Q_{C2H2} =*1.11 sccm and* Q_{Ar} = *10.1 sccm,*
P = 9 W.

If $n_{Ar} \gg n_{C2H2}$, C_2H^- is the dominant anion.
[Schweigert I V, Alexandrov A L and Ariskin D A 2014 Plasma Chem. Plasma Process. **34** 671; Akhoundi A and Foroutan G 2017 Phys Plasmas **24** 053516]

The velocity space of electrons is nearly isotropic and the EEPF is

$$F(\varepsilon) = A_1 \exp(-A_2 \varepsilon^{x_F}), \qquad x_F = 1 \quad (Maxwellian),$$

$$x_F = 2 \quad (Druyvesteyn).$$

A_1 and A_2 – functions of the average energy and x_F
[J T Gudmundsson, Plasma Sources Sci. Technol. ***10****(2001) 76–81]*

Further, we assume that *F* has a Druyvesteyn shape (for *Ar* 13.56 MHz plasma with $n_e < 10^{11}$ cm^{-3} and PL > 0.2 Torr×cm [*V. A. Godyak, R. B. Piejak, and B. M. Alexandrovich, Plasma Sources Sci. Technol.* ***1****, 36 (1992)*.]).

If $n_{C2H2} / n_{Ar} \ll 1$, the effect of C_2H_2 on the EEPF is small [*Schweigert I V, Alexandrov A L and Ariskin D A 2014 Plasma Chem. Plasma Process. 34 671*]

The ions, dust particles are assumed to be at gas temperature T_g (300 K).
Ar is the dominant neutral species. $n_{Ar} \approx P/(k_B T_g)$, P = 5 Pa.

The plasma is quasineutral: $\sum_{\alpha} n_{\alpha}^{+} = n_e + n^{-} + |Z_d| n_d$

The balance equation for a species X (ions or neutrals)

$$\frac{\partial n^{(X)}}{\partial t} = \sum_i R_{G,i}^{(X)} - \sum_i R_{L,i}^{(X)}$$

$R_{G,i}^{(X)}$ *- the rate for a generation process*

$R_{L,i}^{(X)}$ *- the rate for a loss process*

The collisional processes in the bulk plasma, the processes on plasma walls and dust particles, as well as the pumping of gas in (***Ar***, ***C_2H_2***) and out of the chamber are included.

The sticking coefficients for collisions with the walls and dust particles for C_2H, H and Ar* are assumed to be 0.9, 0.1 and 1.0.

The power balance equation

$$P_{abs} = P_{coll} + P_w + P_d,$$

P_{abs} - the absorbed power (in the experiment, P_{abs} = 9 W), P_{coll} and P_w are the power loss due to elastic and inelastic collisions and the loss due to charged particle fluxes to the walls.

$$P_d = e n_e n_d \pi a_d^2 V \int_{-\phi_s}^{\infty} (1+\phi_s/\varepsilon)\sqrt{2e\varepsilon/m_e}\,F(\varepsilon)\varepsilon^{3/2}\,d\varepsilon$$ is the power loss on the dust.

We accounted for the loss in collisions of electrons with C_2H_2, C_4H_2, H_2 , Ar.

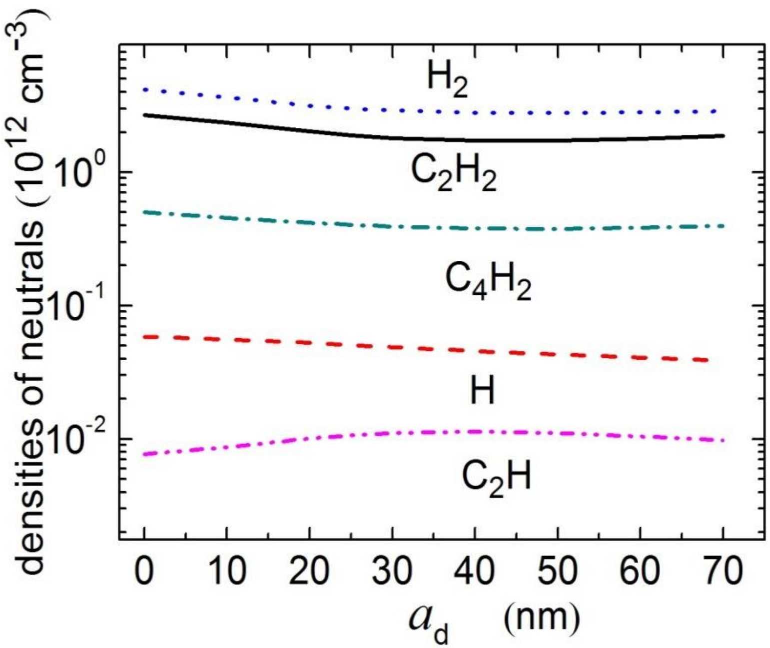
The equation for dust charge $$\frac{\partial |Z_d|}{\partial t} = K_d^e n_e - \sum_\alpha K_d^\alpha n_\alpha^+$$

The deposition of C_2H^- on the walls and dust is not taken into account.

For the afterglow case, we assume that the effective electron temperature decays exponentially according to $T_e(t) = T_{e0}\exp(-t/\tau_T)$

τ_T =50 μs. $T_e \geq 0.1$ eV. At large t, T_e =0.1 eV.

Steady-state plasma. Effect of dust particles.



C_2H_2 and H_2 are the dominant molecules, in agreement with our experiment.

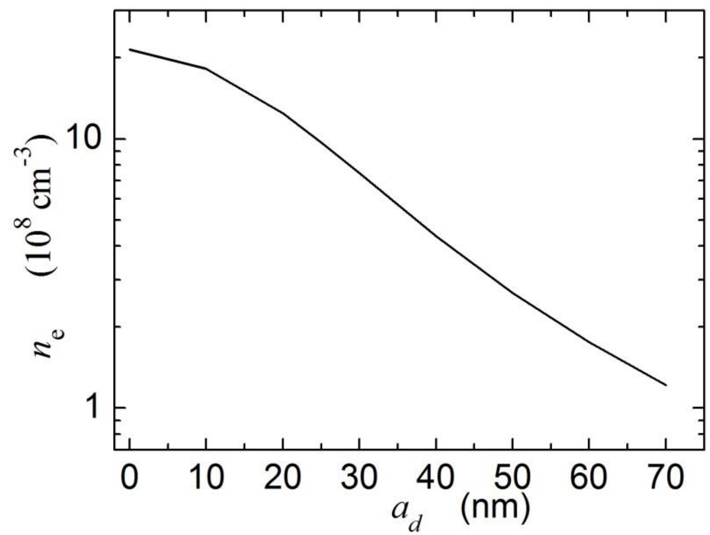
For $n_d=0$, n_{Ar} ($\approx 1.21\times10^{15}$ cm^{-3}) is 453 times larger than n_{C2H2} ($\approx 2.67\times10^{12}$ cm^{-3}) and the degree of dissociation of C_2H_2 is nearly 98 %. [in agreement with *Stefanović I, Sadeghi N and Winter J 2010 J. Phys. D, V. 15, 2003*].

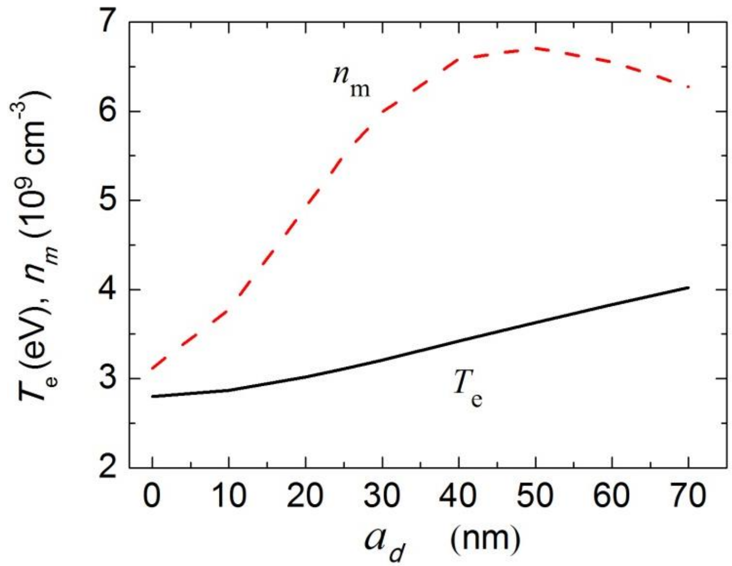
The loss of C_2H_2 is mainly due to their collisions with excited atoms, positive ions, C_2H radicals and electrons. Since for $a_d \leq 50$ nm, the increase of a_d is accompanied by increasing the densities of Ar+ and Ar* and T_e, the density of C_2H_2 decreases. At large a_d, there is a small increase (because of n_e and n* decrease).

The C_4H_2 and H_2 production is related to the C_2H_2 density [*Herrendorf A P, Sushkov V and Hippler R 2017 J. Appl. Phys.* ***121*** *123303*], and as, a result, the a_d - dependencies for C_4H_2 and H_2 densities are similar to that for $n_{C2H2.}$

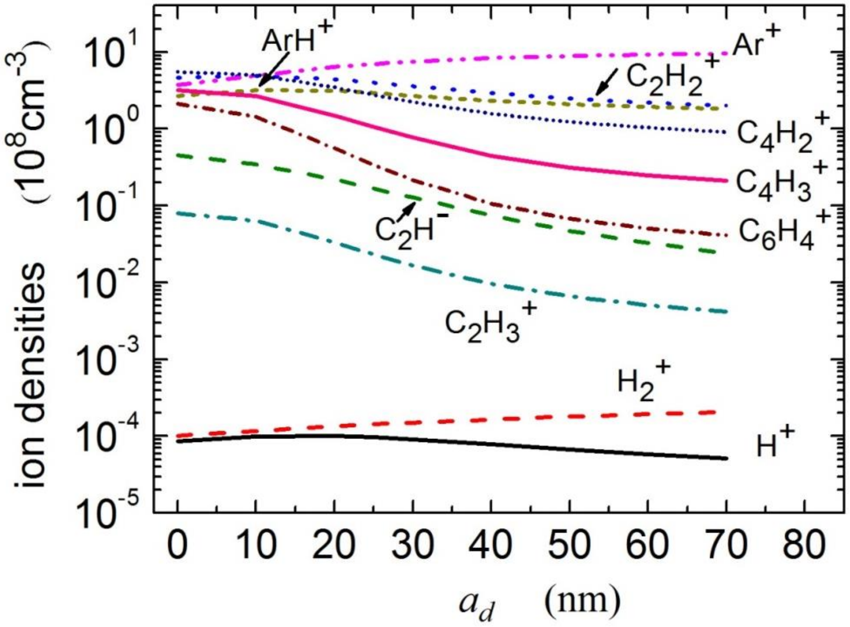
- The decrease of n_H with a_d is due to increasing the loss of H on dust particles and due to the decrease of densities of nonradical molecules and e^- (which take part in production of H).

- The dependence of n_{C2H} on a_d is determined mainly by the a_d-dependencies for densities of Ar* and C_2H_2 (the production: $Ar^* + C_2H_2 \rightarrow C_2H + Ar + H$).





- Because of collection of electrons by dust particles, n_e decreases with increasing a_d , while T_e increases.
- The metastable atom density increases with an increase of a_d for $a_d \le 50$ nm and decreases at larger dust radii. The increase is due to the enlargement of T_e, while the decrease is mainly due to the n_e decrease.

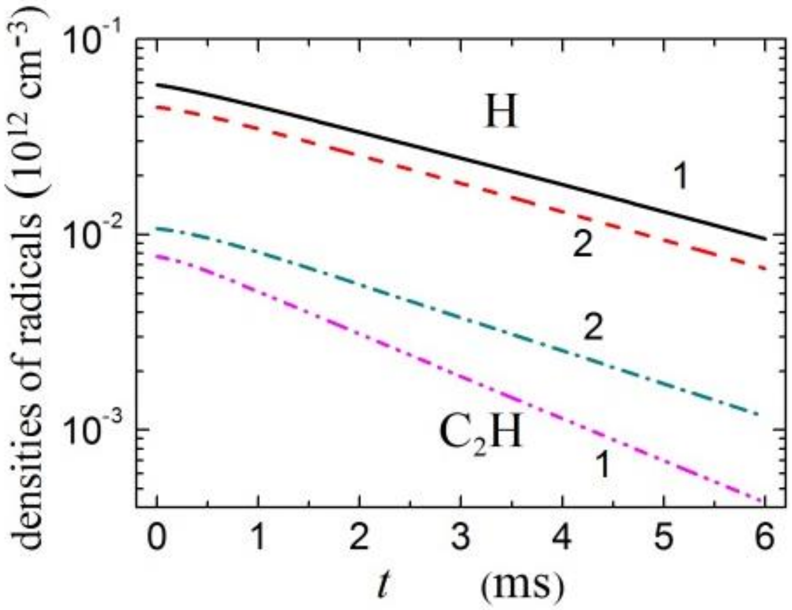


Ar^+, $C_2H_2^+$, $C_4H_2^+$, $C_4H_3^+$, $C_6H_4^+$, ArH^+ - the dominant ions. This agrees well with our measurements.

The densities of H_2^+ and H^+ are smaller than those of the dominant ions (intensive loss in collisions with Ar and C_2H_2, cross-sections for their production are smaller than that for $C_2H_2^+$ [*De Bleecker K, Bogaerts A and Goedheer W 2006 Phys. Rev. E* ***73*** *026406*]).

The densities of Ar^+ and H_2^+ increase with a_d, while the densities of other ions including $C_2H_2^+$ are decreasing. The variations are mainly due to changes in n_e, T_e.

As ground-state Ar atoms have a larger ionization threshold energy than C_2H_2 molecules, the increase of T_e favors Ar^+ production. The H_2^+ density increase is mainly due to the enhancement of H_2^+ production in collisions of Ar^+ with H_2.



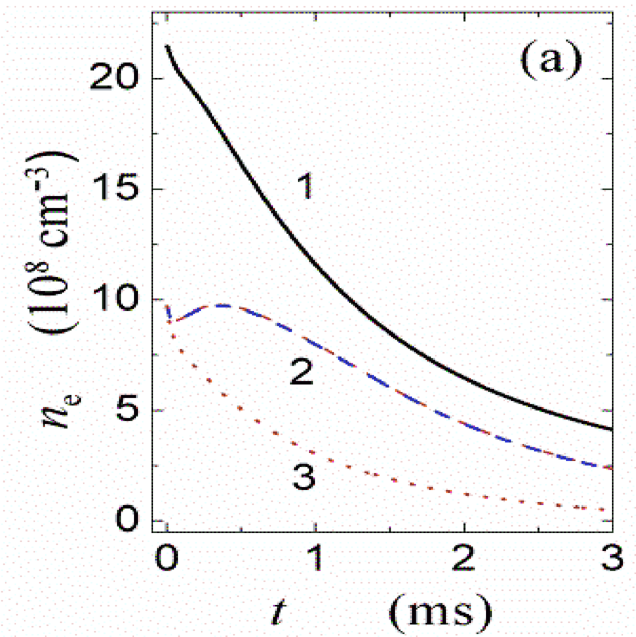
The afterglow plasma

1- the dust-free case
2- the dusty plasma case
a_d=25 nm, n_d =10^7 cm^{-3}

more intensive loss of C_2H in dust-free plasma ($C_2H + C_2H_2 \rightarrow C_2H_2 + H$)

The main loss of *H* is due to diffusion to the walls (the decay times are nearly the same in the $n_d = 0$ and $n_d \neq 0$ cases).

The frequencies characterizing the loss and production of nonradical species, C_2H_2, H_2 and C_4H_2, are small and, as a result, the times characterizing variations of these species are large. Therefore, the densities of nonradical species are nearly independent on time in the ms range. The difference in densities at $t = 0$ and $t = 6$ ms is nearly 2.0%, 0.4% and 0.6%, respectively.



The dust-free (curve 1)
and dusty-plasma cases:
when the electron generation in Ar_m- C_2H_2 collisions ($Ar_m + C_2H_2 \rightarrow C_2H_2^+ + Ar + e^-$) is taken into account (curve 2) and neglected (curve 3).

The results are in qualitative agreement with experiments.

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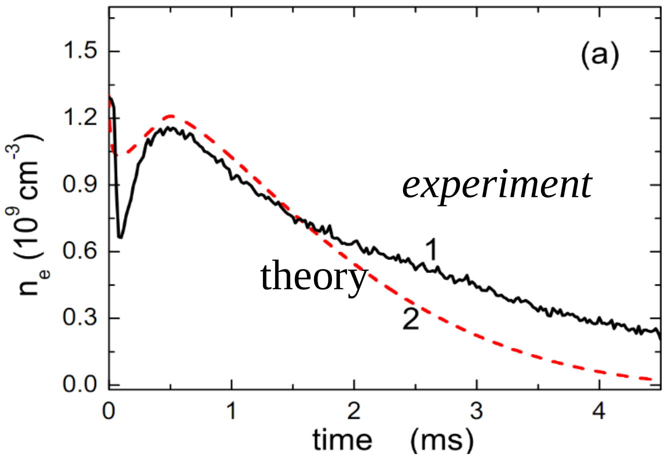
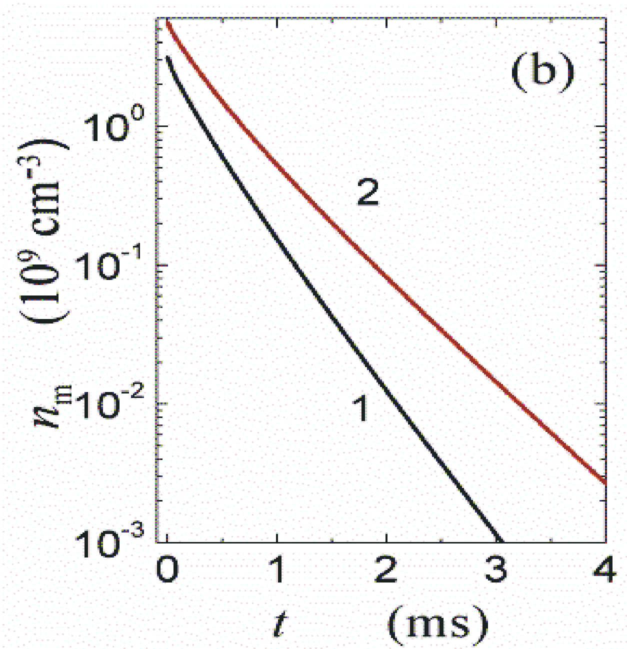
Ar dusty plasma



$n_e(t)$ for a_d = 50 nm, $n_d = 2{,}9\times10^7$ cm^{-3}, p = 0.1 mbar, T_g = 366 K, and $\gamma_i = \gamma_m$ = 0.01. The secondary emission yield γ_i is taken to be the same as that for a stainless steel covered by dust particles *[I. Stefanovic, J. Berndt, D. Maric, V. Samara, M. Radmilovic-Radjenovic, Z. L. Petrovic, E. Kovacevic, and J. Winter, Phys. Rev. E* ***74****, 026406 (2006).].*

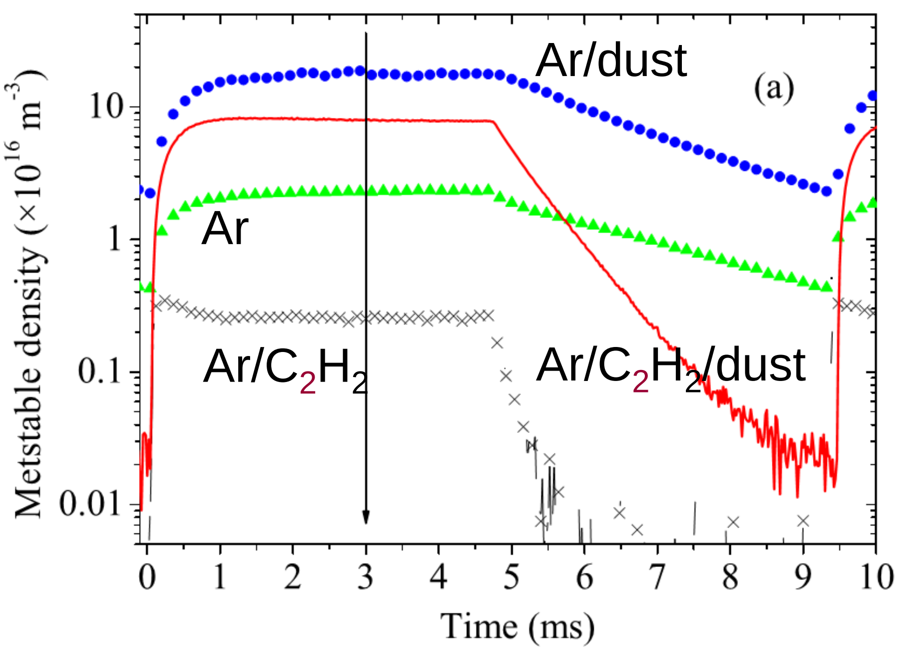
The presence of a peak in the time-dependence for n_e in the case of Ar dusty afterglow was explained by the release of free electrons from the dust particles [*Stefanovic et. al*]

and/or by the electron generation in metastable-metastable collisions [*Denysenko I, Stefanović I, Sikimić B, Winter J, Azarenkov N A and Sadeghi N A 2011 J. Phys. D: Appl. Phys.* ***44*** *205*].



n_m decreases more slowly in the dusty-plasma afterglow (2) as comparing with the $n_d = 0$ case (1) because the metastable losses in the afterglows are mainly due to their collisions with C_2H_2, H_2 and C_4H_2 . Here, the external parameters are for our experiment.

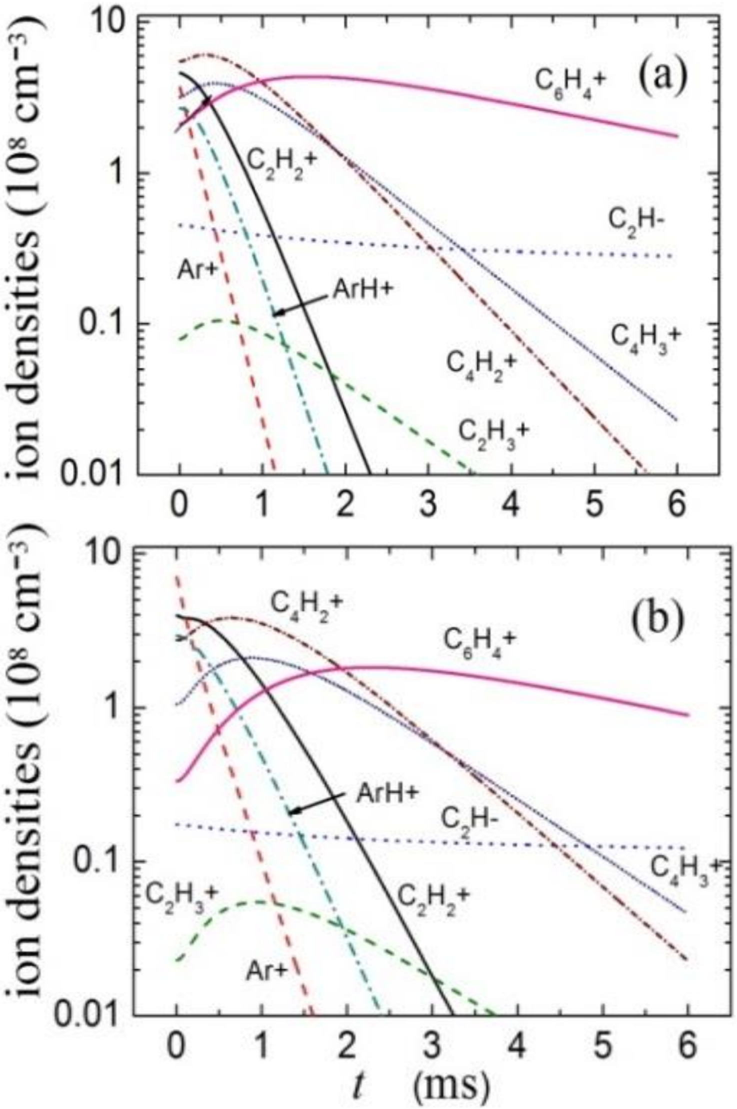
The results are in agreement with experiments.



The dependencies for n_m from *Stefanović et al. 2017 Plasma Sources Sci. Technol.* ***26*** *065014*

The decrease of Ar_m density in Ar/dusty plasma is mainly due to diffusion to the walls and collisions with dust.

Densities of ions in the dust-free (a) and dusty-plasma (b) afterglows as functions of *t*



The decay time for Ar^+ is smaller than that for other ions because the production of Ar^+ ions is only due to electron-neutral collisions, while other ions are also produced in collisions of neutrals with ions and/or metastable atoms.

For the $C_2H_2^+$, Ar^+ and ArH^+ ions, the main loss mechanism is due to the collisions with nonradical neutrals (do not change much in the afterglow).

The diffusion to the walls is one of the main loss process for $C_2H_3^+$, $C_4H_2^+$, $C_4H_3^+$ and $C_6H_4^+$, the losses decrease rapidly [T_e(t)]. *The production may dominate over the ion loss and, the ion densities increase with increasing t.*

The densities of Ar^+, $C_2H_2^+$, ArH^+, $C_2H_3^+$, $C_4H_2^+$ and $C_4H_3^+$ decrease faster with increasing *t* in the dust-free case (larger densities of C_2H_2 and H_2 .

It is assumed that the anions do not deposit on the walls and dust. n^- decreases slowly.

Recent publications

1) IB Denysenko, NA Azarenkov, K Ostrikov, MY Yu, Electron energy probability function in the temporal afterglow of a dusty plasma, Physics of Plasmas 25, 013703 (2018).
2) I B Denysenko, E von Wahl, S Labidi, M Mikikian, H Kersten, T Gibert, E Kovačević and N A Azarenkov , *Plasma Phys. Control. Fusion* 61, 014014 (2019).
3) *Igor B. Denysenko, Kostya (Ken) Ostrikov and Nikolay A. Azarenkov, Book Chapter 1:"* MODELLING OF PLASMA-ASSISTED GROWTH OF VERTICALLY ALIGNED CARBON NANOSTRUCTURES" 1-59, IN Advances in Materials Science Research. Volume 34, M. C. Wythers(Editor), October 2018, 242 pages, Nova Science Publishers.

Summary

- We have analysed by a spatially-averaged model how dust particles affect the properties of glow and afterglow Ar/C_2H_2 plasmas.

- For the glow plasma case, the densities of C_2H_2, H_2 and C_4H_2 at the same external conditions are smaller in the dusty plasma than in the n_d=0 case due to the enhancement of their loss in various collisional processes. This enhancement is mainly due to the increasing of the effective electron temperature caused by collection of electrons by the dust.

- The temperature increase is accompanied by more intensive production of Ar^+ ions and, as a result, by an increase of their density. Meantime, due to enhanced collection of electrons and ions by dust particles, the densities of most hydrocarbon ions decrease with increasing the dust radius.

- Because of the competition between the increase of T_e and the decreasing of n_e, the metastable atom density grows with increasing a_d at moderate dust radii (here, a_d < 50 nm) and decreases at larger dust radii.

- The dust particles also affect the radical, ion and electron densities and the density of metastable argon atoms in the Ar/C_2H_2 plasma afterglow.

- Since the density of acetylene molecules is larger in a dust-free plasma than in the dusty one, the densities of C_2H radicals, most positive ions and metastable argon atoms decrease more rapidly in the afterglow, because of their more intensive loss in collisions with nonradical neutrals.

- Due to large density of argon metastable atoms in the dusty plasma, the electron production from collisions between metastable atoms and C_2H_2 molecules is intensive leading to a possible peak in $n_e(t)$ during the afterglow.

- The results of numerical calculations are in a good qualitative agreement with our experimental results on glow Ar/C_2H_2 plasma and afterglow plasmas from the literature.

Thank you very much for your attention!!!   *Дякую за увагу !!!*