Journal of Physics D: Applied Physics

Sterilization and decontamination of medical instruments by low-pressure plasma discharges: application of $Ar/O_2/N_2$ ternary mixture

To cite this article: O Kylián and F Rossi 2009 *J. Phys. D: Appl. Phys.* **42** 085207

J. Phys. D: Appl. Phys. **42** (2009) 085207 (7pp) doi:10.1088/0022-3727/42/8/085207

Sterilization and decontamination of medical instruments by low-pressure plasma discharges: application of $Ar/O_2/N_2$ ternary mixture

O Kylián[1] and F Rossi[2]

[1] Charles University, Faculty of Mathematics and Physics, V Holešovičkách 2, Prague 8, 180 00, Czech Republic
[2] European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Via E Fermi 2749, 21027 Ispra (VA), Italy

E-mail: francois.rossi@jrc.it

Received 16 January 2009, in final form 26 February 2009
Published 2 April 2009
Online at stacks.iop.org/JPhysD/42/085207

Abstract
A low-pressure inductively coupled plasma discharge sustained in an argon–oxygen–nitrogen ternary mixture is studied in order to evaluate its properties in terms of sterilization and decontamination of surfaces of medical instruments. It is demonstrated by direct comparison with discharges operated in oxygen–nitrogen and oxygen–argon mixtures that application of an $Ar/O_2/N_2$ mixture offers the possibility to combine advantageous properties of the binary mixtures, namely, the capability of an O_2/N_2 plasma to emit intense UV radiation needed for effective inactivation of bacterial spores together with high removal rates of biological substances from Ar/O_2 discharge. Moreover, optimal conditions for both effects are obtained at a similar ternary discharge mixture composition, which is of much interest for real applications, since it offers a highly effective process desired for the safety of medical instruments.

1. Introduction

Cleaning, sterilization and decontamination of medical equipment are fundamental steps in health care facilities in order to assure safety of patients. However, there are numerous indications that currently used techniques are in many cases insufficient to guarantee complete inactivation or elimination of various pathogens (e.g. [1–5]); this consequently represents a serious problem mainly with respect to the possible transmission of lethal neurodegenerative diseases or the onset of immunological events of severe consequences caused by insufficiently cleaned instruments. Therefore, there is a clear demand from hospitals' sterile services for the development of alternative methods allowing complete elimination of highly resistant biological residues possibly present on the surfaces of medical tools. One of the options that gained increased attention in the last decade is the application of low-pressure, non-equilibrium plasma discharges that are capable of not only inactivating bacteria or bacterial spores (e.g. review papers [6–9]) but also eliminating bacterial endotoxins [9–11] or removing protein residuals (e.g. [9, 12–19]), i.e. substances that are difficult or impossible to remove by other techniques. Therefore, the possibility to assure sterility and complete elimination of biological pathogens from the surfaces of medical instruments makes the plasma based sterilization/decontamination technique one of the most promising approaches to fulfil requirements on a universal sterilization/decontamination method. However, as will be discussed in the following section, the conditions leading to inactivation of bacteria or physico-chemical removal of biological residues are different: while a maximum of UV emission is desirable in the first case, a maximum concentration of active species necessary for etching the residues is needed in the second case. The main intention of this paper is to demonstrate that both of these features can be achieved by the application of low-pressure inductively coupled plasma

(ICP) discharges sustained in a $Ar/O_2/N_2$ ternary gas mixture. To do so, the paper is organized as follows. First, the recent results regarding the possible approaches used for the inactivation of bacterial spores on the one hand and physical removal of biomolecules from surfaces on other hand are briefly summarized in section 2. The experimental set-up and methods used in the frame of this study are introduced in section 3. Finally, the results of this study are presented and discussed in section 4 and concluded in section 5.

2. Overview of approaches used for sterilization and decontamination of surfaces

Concerning recent results, two distinct strategies applicable for the sterilization and decontamination of surfaces by means of low-pressure plasma discharges can be followed.

The first one relates to the possibility to remove physically all kinds of pathogens by etching or sputtering. This is traditionally achieved by placing objects to be treated in the active zone of the discharges providing sufficient fluxes of etching agents or energetic ions that can either sputter treated samples or enhance their elimination via the process of chemical sputtering involving both charged particles and plasma radicals [20–22]. Although it has been demonstrated that bacterial spores or biomolecules can be removed from surfaces, or at least significantly eroded, using a wide range of gases, a majority of the research groups use different oxygen containing plasma discharges (e.g. pure oxygen [23–26], O_2/H_2 [9, 11, 18], O_2/N_2 [27], He/O_2 [15, 16] or Ar/O_2 [13, 17, 19]), which offer high removal rates, as demonstrated, for instance, by SEM images of treated bacteria [25–28] or proteins [29], but do not represent environmental risks as for example fluorine mixtures known to be also highly effective in etching of polymers (e.g. [30]). Nevertheless, it has to be noted that the approach based solely on the physico-chemical removal of pathogens, which at first glance seems to be an optimal and universal sterilization/decontamination method, has also certain limitations especially with respect to the inactivation of bacterial spores. It has been demonstrated that spores etching is much slower as compared with various biomolecules treated at otherwise identical operational conditions (e.g. [23]) and it is rather challenging to etch spores completely [30]. This is due to the high amount of inorganic compounds (e.g. calcium, sodium, etc) presented in the spores' walls. Such compounds are difficult to volatilize and therefore their fraction increases with treatment time, which leads to the formation of highly resistant inorganic layer and consequently to the slowing down of the removal rate. As a result of this, prolonged treatments are necessary, which can lead to extensive heating and degradation of treated objects.

The second approach used is based on the induction of chemical or structural modifications of treated pathogens leading to the suppression of their biological activity. Although it has been demonstrated that certain biomolecules can be inactivated in this way (concretely bacterial endotoxins [31]), this approach refers mainly to the sterilization of bacterial spores. According to the conclusions stated in recent papers, the most effective sporicidial agent in low-pressure plasma discharges is intense UV radiation (typically in the spectral range 200–300 nm [32, 33]) capable of penetrating the spores' outer walls and of inducing irreversible modifications of their DNA. The most commonly used discharge mixture to generate UV radiation is oxygen–nitrogen mixture, where the main source of photons in the desired spectral range constitute excited NO molecules. Moreover, excited NO molecules can be effectively produced also in the plasma discharge afterglows, which is mainly due to three body reaction involving atomic oxygen, nitrogen and N_2 molecules [34]:

$$N + O + N_2 \rightarrow NO(A) + N_2. \qquad (1)$$

This allows objects to be sterilized to be placed downstream of the active plasma discharge zone while still maintaining a sufficient flux of UV photons and lowering the risk of possible damage of treated articles induced either by extensive heating or by the impact of chemically aggressive radicals.

However, optimizing only UV radiation or placing samples in the afterglow also has serious drawbacks, since it does not typically provide fast removal of biological agents from surfaces due to the low fluxes of chemically active species as well as due to the absence of charged particles that contribute significantly to the process of volatilization of biological systems [20–22]. Not only is this a limitation in terms of removal of pathogenic biomolecules such as infectious proteins or endotoxins but it also influences the overall efficiency of bacterial spores sterilization. Often the spores are stacked or covered with other biological substances, which represents a protective shield towards UV radiation and naturally slows down the sterilization effect of UV radiation. This can be, for instance, demonstrated on the survival curves of bacterial spores obtained in low-pressure discharge plasmas showing typically two phases—the first and the faster phase corresponds to the fast inactivation of spores that are in a direct view of UV radiation; the second phase, and a markedly slower one, is then connected to the killing of covered spores that needs a much longer time to accumulate lethal UV dose [35] and/or with gradual, and rather slow, removal of the shielding material through photo-desorption [6], etching or chemical sputtering.

Therefore, it is clear that an optimal sterilization/decontamination process should combine both the above-mentioned pathways, i.e. providing conditions offering *both* high intensity of UV radiation favourable for fast inactivation of spores *and* high removal rates of possible pathogens or materials shielding spores from direct action of UV radiation. This is commonly fulfilled using an O_2/N_2 mixture and placing objects to be treated in the active zone of the discharge (e.g. [27, 33]). However, it has been recently suggested that the desired effect can also be reached by the application of an Ar/NO discharge mixture [36] or utilizing a ternary mixture consisting of argon, oxygen and nitrogen [37]. In this paper the second option is followed. In order to show the advantageous properties of ternary mixtures, their capability to remove model biomolecules and to emit intense UV radiation in the range 235–270 nm will be compared directly with discharges sustained in O_2/N_2 and Ar/O_2 mixtures, i.e. mixtures identified to be optimal for UV radiation and elimination of biomolecules, respectively.

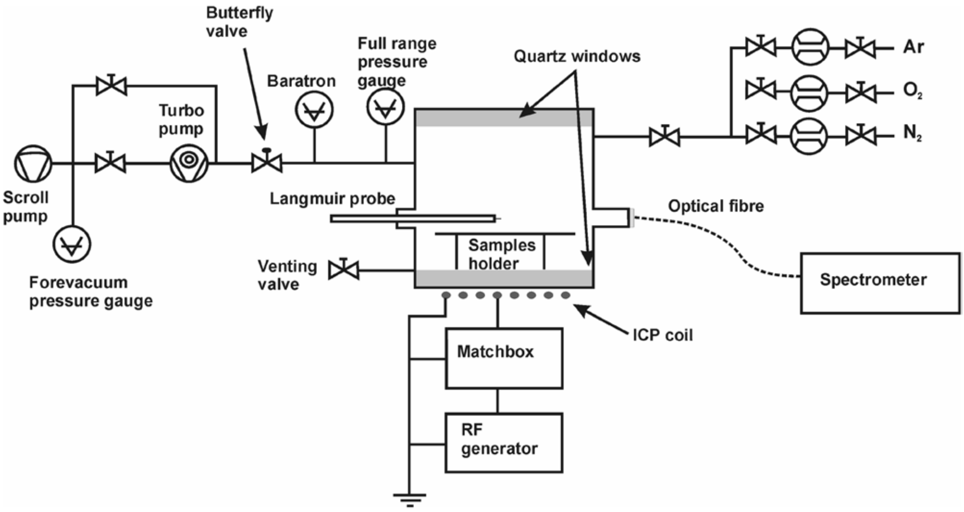

Figure 1. Experimental set-up.

3. Experimental

3.1. Discharge chamber

An ICP source schematically depicted in figure 1 was used in this study. The plasma discharges sustained in O_2, N_2, Ar and their binary and ternary mixtures (pressure 10 Pa, total gas flow 20 sccm and, if not stated otherwise in the text, applied RF power 350 W) were characterized by optical emission spectroscopy using an Avantes AVS-PC2000 monochromator equipped with a 2048-element linear CCD array and by means of a Langmuir probe (SmartProbe™; Scientific Systems Ltd) placed in the sample position.

Moreover, in order to limit the heating of the treated samples, which can significantly influence the kinetics of their etching [38], all the experiments were performed with a treatment duration of 15 s, i.e. the duration after which the substrate temperature measured by IR pyrometry stayed well below 80 °C.

3.2. Samples preparation and characterization

The efficiency of the studied plasma discharges to eliminate biological contamination from surfaces was evaluated on bovine serum albumin (BSA). It has to be noted that although this protein itself is harmless, it serves as a good model of biological contamination of surfaces of medical instruments. The BSA samples were prepared by spotting 0.1% aqueous solution of BSA (Sigma Aldrich) on the polished and cleaned Si wafers. After the deposition, the samples were dried overnight in a common flow hood and subsequently plasma treated. The treated and untreated samples were examined by means of stylus profilometry, which allows direct evaluation of the removal rates of proteins. For the measurements, an Alpha-step® profilometer (KLA-Tencor) was used with a scan speed of 20 μm min^{-1} and a sampling rate of 50 Hz. Equivalent force exerted from the stylus tip on the surface corresponded to 27.4 mg. Details regarding samples preparation and evaluation of etching rates can be found in the literature [19].

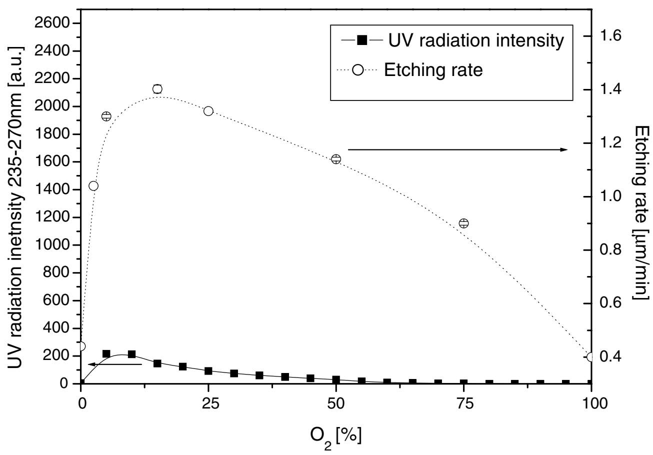

Figure 2. UV radiation intensity integrated in the spectral range 235–270 nm and BSA removal rate as a function of initial argon–oxygen mixture composition (10 Pa, 350 W, total gas flow 20 sccm).

4. Results

4.1. Oxygen containing binary mixtures

In a first step, we evaluated the most suitable discharge mixture in terms of sterilization and decontamination of surfaces by testing the capabilities of plasma discharges sustained in O_2–N_2 and Ar–O_2 mixtures in order to identify their advantages as well as limitations.

4.1.1. Argon–oxygen mixture. As can be seen in figure 2, the ICP discharge sustained in the Ar/O_2 mixture can effectively eliminate the BSA protein. From this perspective the optimal discharge mixture is the one having an argon/oxygen ratio of about 17/3, i.e. the mixture having approximately 15% of oxygen; this mixture produces a removal rate of 1.4 μm min^{-1} for an applied power of 350 W and a pressure of 10 Pa. Increasing either the argon or oxygen portion in the initial discharge mixture leads to a significant decrease in the BSA removal rate. As was demonstrated in previous studies

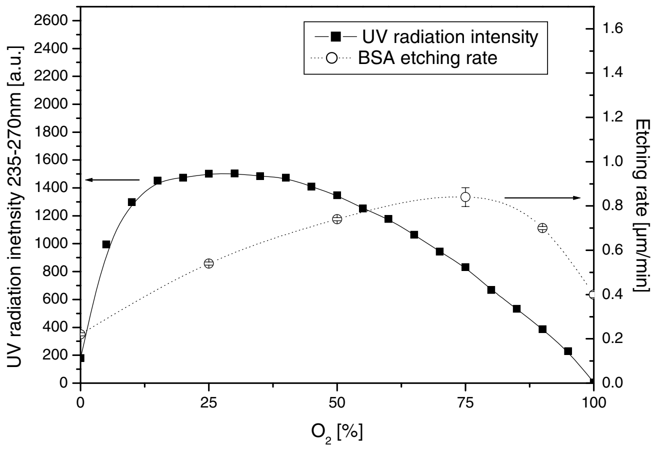

Figure 3. UV radiation intensity integrated in the spectral range 235–270 nm and BSA removal rate as a function of initial oxygen–nitrogen mixture composition (10 Pa, 350 W, total gas flow 20 sccm).

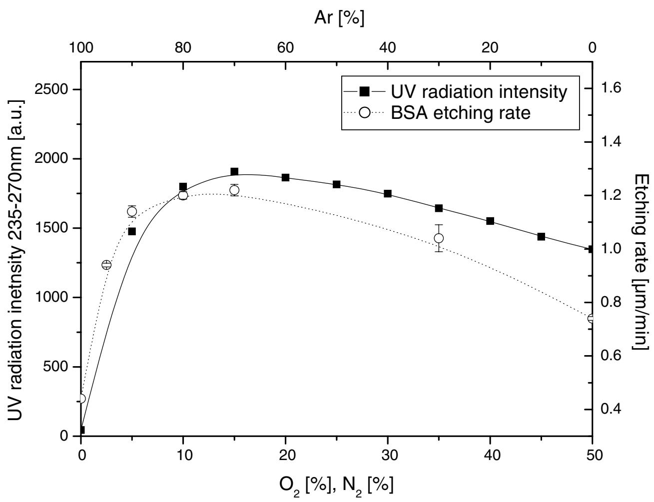

Figure 4. UV radiation intensity integrated in the spectral range 235–270 nm and BSA removal rate as a function of initial argon–oxygen–nitrogen X : 1 : 1 mixture composition (10 Pa, 350 W, total gas flow 20 sccm).

performed under similar experimental conditions [37, 39], the existence of a well-defined maximum of proteins removal rate cannot be interpreted solely by pure chemical etching induced by O atoms, since O atoms density increases monotonically with increasing fraction of O_2 in the mixture as shown both by optical emission actinometry [37] and mass spectroscopy [39]. Instead, the dominant role of chemical sputtering has been suggested in order to explain the observed results. In this reaction scheme the overall rate of BSA elimination is given by the simultaneous action of O atoms and energetic ions produced in the discharge plasma. The variations of the BSA removal rate can consequently be attributed either to the lowering of the flux of atomic oxygen needed for proteins volatilization (in the case of increasing Ar amount) or to a fast decrease in ion density (when the oxygen portion is increased) leading to the reduced rate of chemical sputtering.

Moreover, it can also be seen in figure 2 that Ar/O_2 is a bad source of UV radiation. The low emission observed in the 235–270 nm spectral range originates only from a small amount of nitrogen impurities present in the discharge chamber.

4.1.2. Oxygen–nitrogen mixture. As expected, much better results concerning UV radiation are observed using the O_2/N_2 discharge mixture. As can be seen in figure 3, the O_2/N_2 mixture offers almost one order of magnitude higher UV radiation intensity as compared with Ar/O_2. However, the removal rate of BSA using the O_2/N_2 mixture is considerably smaller than the values reached using the Ar/O_2 discharge (maximal removal rate observed in the O_2/N_2 plasma discharge is 0.84 μm min^{-1}, which is 40% lower as compared with the one observed using Ar/O_2). It is worth mentioning that unlikely to the argon–oxygen mixture, the variations of the BSA etching rate can be attributed solely to the changes in fluxes of active oxygen, since no significant variations of ion density were observed with changing the oxygen/nitrogen ratio in the initial discharge mixture, as will be demonstrated later. Moreover, it can be seen that the maximal values of the removal rate of BSA and the intensity of UV radiation are obtained at markedly different mixture compositions: the highest rate of protein removal was observed for mixture having around 80% of O_2, whereas the maximal UV intensity in the spectral range 235–270 nm can be achieved for fraction 20–30% of O_2 in the Ar/O_2 plasma. In other words, changing the O_2/N_2 ratio leads either to enhancement of UV light emission and decrease in capability of oxygen–nitrogen plasma discharge to eliminate biomolecules or vice versa.

4.2. Ar/N_2/O_2 ternary mixture

As was demonstrated above, discharges sustained in binary mixtures can be operated at conditions *either* favourable for the elimination of biomolecules *or* suitable for the emission of intense UV radiation. Moreover, the direct comparison of Ar/O_2 and N_2/O_2 discharges revealed that the first one offers a markedly higher rate of biomolecules removal, whereas the second one can be used as an effective source of UV radiation. In order to explore the possibility to combine these two properties, further experiments were performed in Ar/N_2/O_2 ternary mixture with fixed O_2 over N_2 ratio 1 : 1 and varying Ar portion in the discharge mixture, while keeping the total gas flow constant. As can be seen in figure 4, substitution of oxygen and nitrogen by argon up to 80% of Ar leads to the increase in *both* UV radiation intensity *and* BSA removal rate. Further increase in the Ar fraction in the discharge mixture subsequently causes a decrease in these two quantities. However, it is evident that these results are rather advantageous as compared to Ar/O_2 and N_2/O_2 binary discharge mixtures:

- First, the application of Ar/N_2/O_2 ternary mixture maintains a high removal rate of BSA (maximal value observed is approximately 1.2 μm min^{-1}) still comparable to the one obtained in the Ar/O_2 discharge and leads to the emission of UV radiation having an intensity even higher than the maximal one reachable at identical operational conditions (i.e. pressure, RF power and total gas flow) in the case of the nitrogen–oxygen plasma.

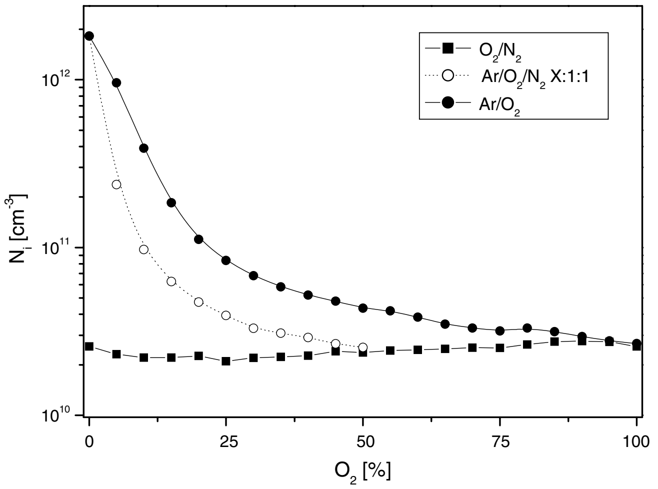

Figure 5. Positive ion density in studied discharge mixtures (10 Pa, 350 W, total gas flow 20 sccm).

- Second, the maximal values of both the protein removal rate and UV radiation intensity are obtained for similar discharge mixture compositions. This is a result of considerable importance, since it allows overcoming the principal drawback of discharges sustained in oxygen–nitrogen binary discharge mixture demonstrated in the previous section, i.e. the possibility to maximize either the UV intensity or the removal rate of biological systems.

The results obtained are most likely connected not only with the behaviour of the density of neutral species produced in the plasma but also with the variation of the plasma density. As can be seen in figure 5, argon addition into oxygen–nitrogen discharge mixture leads to an increase in plasma density similarly to the increase observed with increasing fraction of Ar in Ar/O_2 plasma. This effect is due to higher electron energy losses in interactions with molecular gases than with argon atoms (e.g. [40]). In other words, the energy supplied to the discharge is consumed in the case of molecular gases not only for their ionization but also for their vibrational and rotational excitations. Lowering the amount of molecular gases in the initial discharge mixture therefore reduces these energy losses and subsequently more energy is available for ionization, which results in a higher plasma density, which has important practical consequences:

First, the higher flux density of ions on the treated surfaces promotes the process of its chemical sputtering by enhanced rate of breaking of molecular bonds in the protein deposit by impinging ions, thus creating more surface active sites that are subsequently attacked by plasma produced radicals. This can explain the observed increase in the BSA removal rate when argon is added into the oxygen–nitrogen mixture in analogy to the case of Ar/O_2 plasma discharge as described for the cases of bacterial spores and hydrocarbon films [39].

Second, higher production of charged particles increases the production of electronically excited species. This can be demonstrated, for instance, on the behaviour of the intensities of the first and second positive systems of molecular nitrogen measured in O_2/N_2 and $Ar/O_2/N_2$ plasma discharges. As can be seen in figure 6, the intensity of these two spectral bands decreases monotonically with increasing oxygen over nitrogen ratio in the O_2/N_2 mixture, which is, taking into account almost constant plasma density, mainly due to the decrease in the N_2 portion in the plasma discharge. This trend is significantly altered when argon is added into the discharge mixture—intensities of both nitrogen spectral bands increase with decreasing N_2 amount, reflecting an increase in the density of nitrogen molecules in their higher electronically states. Although both $N_2(B)$ or $N_2(C)$ states do not contribute to the production of excited NO molecules responsible for the emission of UV radiation, one can expect similar tendencies also for $N_2(A)$ states that are strongly linked to the densities of the $N_2(B)$ molecules [41] and that were identified to play a dominant role for the production of $NO(A)$ molecules in the active zone of the discharge through reaction (e.g. [42, 43])

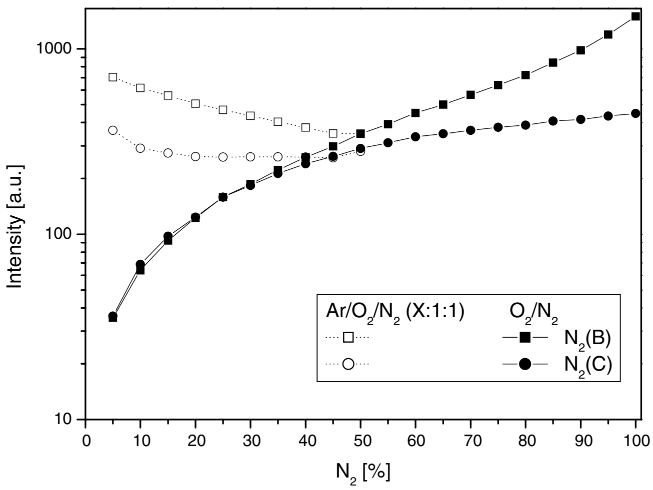

Figure 6. Intensity of the first positive system $N_2(B)$ and the second positive system $N_2(C)$ of molecular nitrogen as a function of nitrogen fraction in the initial discharge mixture (10 Pa, 350 W, total gas flow 20 sccm).

$$NO + N_2(A) \rightarrow NO(A) + N_2 \qquad (2)$$

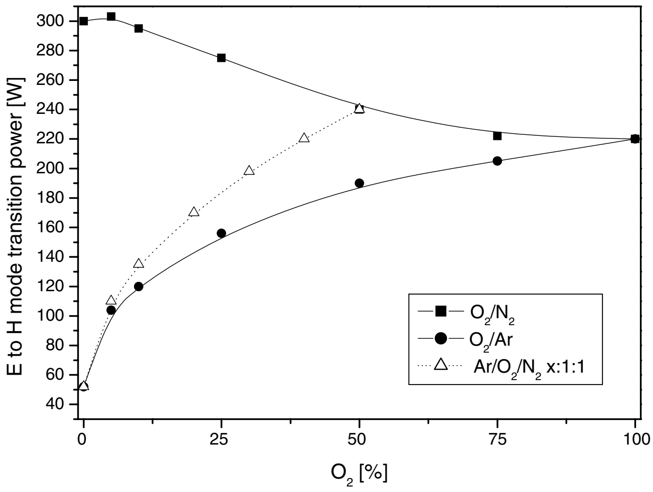

Figure 7. E to H mode transition power in studied discharge mixtures (10 Pa, total gas flow 20 sccm).

as well as to contribute to the process of creation of ground state NO molecules [41]:

$$N_2(A) + O \rightarrow NO + N(^2D). \quad (3)$$

The higher production of $N_2(A)$ resulting from the higher electron density can therefore explain the more effective excitation of NO molecules and consequently the higher intensity of NOγ spectral bands in the spectral range 235–270 nm in Ar/O_2/N_2 plasma discharges than in the oxygen–nitrogen one.

Moreover, higher plasma density in argon containing mixtures as compared with O_2/N_2 plasma discharge also has practical consequences for process optimization: it lowers the power transition point between E and H modes of ICP discharges, i.e. modes characterized by prevailing capacitive (E-mode) or inductive (H-mode) coupling [44], as depicted in figure 7. This allows decreasing the applied RF power maintaining high treatment efficiency connected with the H-mode [23] on the one hand and lowering the thermal load on the other hand. Especially the latter is of high interest from the point of view of the real applications, where thermo-labile materials have to be processed.

5. Conclusions

In summary, two different aspects of plasma discharges, namely, their capability to emit UV radiation in the spectral range suitable for fast inactivation of bacterial spores and efficiency of removal of model biological substance, were studied in order to explore the possibility to use Ar/O_2/N_2 discharge mixture for sterilization and decontamination of surfaces. The results presented clearly show that under otherwise identical operational conditions (RF power, pressure and total gas flow), discharges sustained in the ternary mixture of argon, oxygen and nitrogen combine advantageous properties of plasma discharges operated in O_2/N_2 and Ar/O_2 mixtures. This allows reducing the applied RF power fed to the discharge or to significantly shorten the treatment time necessary for the assurance of the safety of processed medical tools, which in turn limits undesirable damage induced by plasma action on treated articles. The observed results were furthermore related to the behaviour of plasma density that has been suggested to be the major agent governing both the production of UV radiation and the removal of BSA protein deposits, selected as a model of biological contamination of the surface.

Acknowledgments

This work has been supported by the FP6 2005 NEST project ‘Biodecon’ and the JRC Action 15008: NanoBiotechnology for Health.

References

[1] Miller D M, Youkhana I, Karunaratne W U and Pearce A 2001 *Anaesthesia* **56** 1069
[2] Dinakaran S and Kayarkar W 2002 *Eye* **16** 281
[3] Lipscomb I P, Sihota A K and Keevil C W 2006 *J. Clin. Microbiol.* **44** 3728
[4] Murdoch H, Taylor D, Dickinson J, Walker J T, Perrett D, Raven N D H and Sutton J M 2006 *J. Hosp. Infect.* **63** 432
[5] Baxter R L, Baxter H C, Campbell G A, Grant K, Jones A, Richardson P and Whittaker G 2006 *J. Hosp. Infect.* **63** 439
[6] Moisan M, Barbeau J, Moreau S, Pelletier J, Tabrizian M and Yahia L’H 2001 *Int. J. Pharm.* **226** 1
[7] Lerouge S, Fozza A C, Wertheimer M R, Marchand R and Yahia L’H 2000 *Plasma polym.* **5** 31
[8] Laroussi M 2005 *Plasma Process. Polym.* **2** 391
[9] Rossi F, Kylián O and Hasiwa M 2006 *Plasma Process. Polym.* **3** 431
[10] Kylián O, Hasiwa M and Rossi F 2006 *IEEE Trans. Plasma Sci.* **34** 2606
[11] Hasiwa M, Kylián O, Hartung T and Rossi F 2008 *Innate Immun.* **14** 89
[12] Mogul R, Bol’shakov A A, Chan S L, Stevens R M, Khare B N, Meyyappan M and Trent J D 2003 *Biotechnol. Prog.* **19** 776
[13] Baxter H C, Campbell G A, Richardson P R, Jones A C, Whittle I R, Casey M, Whittaker A G and Baxter R L 2006 *IEEE Trans. Plasma Sci.* **34** 1337
[14] Bernard C, Leduc A, Bardeau J, Saoudi B, Yahia L’Y and De Crescenzo G 2006 *J. Phys. D: Appl. Phys.* **39** 3470
[15] Deng X T, Shi J J, Chen H L and Kong M G 2007 *Appl. Phys. Lett.* **90** 013903
[16] Deng X T, Shi J J and Kong M G 2007 *J. Appl. Phys.* **101** 074701
[17] Baxter H C, Campbell G A, Whittaker A G, Jones A C, Aitken A, Simpson A H, Casey M, Bountiff L, Gibbard L and Baxter R L 2005 *J. Gen. Virol.* **86** 2393
[18] Ceccone G, Gilliland D, Kylián O and Rossi F 2006 *Czech. J. Phys.* **56** B672
[19] Kylián O, Rauscher H, Gilliland D, Brétagnol F and Rossi F 2008 *J. Phys. D: Appl. Phys.* **41** 095201
[20] Opretzka J, Benedikt J, Awakowicz P, Wunderlich J and von Keudell A 2007 *J. Phys. D: Appl. Phys.* **40** 2826
[21] Raballand V, Benedikt J, Wunderlich J and von Keudell A 2008 *J. Phys. D: Appl. Phys.* **41** 115207
[22] Kylián O, Benedikt J, Sirghi L, Reuter R, Rauscher H, von Keudell A and Rossi F 2009 *Plasma Process. Polym.* **6** doi:10.1002/ppap200800199

[23] Rossi F, Kylián O, Rauscher H, Gilliland D and Sirghi L 2008 *Pure Appl. Chem.* **80** 1939
[24] Vicoveanu D, Popesco S, Ohtsu Y and Fujita H 2008 *Plasma Process. Polym.* **5** 350
[25] Nagatsu M , Terashita F, Nonaka H, Xu L, Nagata T and Koide Y 2005 *Appl. Phys. Lett.* **86** 211502
[26] Vujošević D, Mozetič M, Cvelbar U, Krstulović N and Milošević S 2007 *J. Appl. Phys.* **101** 103305
[27] Kylián O, Sasaki T and Rossi F 2006 *Eur. Phys. J. Appl. Phys.* **34** 139
[28] Vratnica Z, Vujoševic D, Cvelbar U and Mozetic M 2008 *IEEE Trans. Plasma Sci.* **36** 1300
[29] Whittaker A G, Graham E M, Baxter R L, Jones A C, Richardson P R, Meek G, Campbell G A, Aitken A and Baxter H C 2004 *J. Hosp. Infect.* **56** 37
[30] Lerouge S, Wertheimer M R, Marchand R, Tabrizian M and Yahia L'H 2000 *J. Biomed. Mater. Res.* **51** 128
[31] Kylián O, Hasiwa M, Gilliland D and Rossi F 2008 *Plasma Process. Polym.* **5** 26
[32] Halfmann H, Denis B, Bibinov N, Wunderlich J and Awakowicz P 2007 *J. Phys. D: Appl. Phys.* **40** 5907
[33] Xu L, Nonaka H, Zhou H Y, Ogino A, Nagata T, Koide Y, Nanko S, Kurawaki I and Nagatsu M 2007 *J. Phys. D: Appl. Phys.* **40** 803
[34] Kutasi K, Saoudi B, Pintassilgo C D, Loureiro J and Moisan M 2008 *Plasma Process. Polym.* **5** 840
[35] Philip N, Saoudi B, Crevier M C, Moisan M, Barbeau J and Pelletier J 2002 *IEEE Trans. Plasma Sci.* **30** 1429
[36] Hueso J L, Rico V J, Frías J E, Cotrino J and Gonzáles-Rlipe A R 2008 *J. Phys. D: Appl. Phys.* **41** 092002
[37] Stapelmann K, Kylián O, Denis B and Rossi F 2008 *J. Phys. D: Appl. Phys.* **41** 192005
[38] Cvelbar U, Vujoševic D, Vratnica Z and Mozetic M 2006 *J. Phys.D: Appl. Phys.* **39** 3487
[39] Benedikt J, Flötgen C, Kussel G, Raballand V and von Keudell A 2008 *J. Phys.: Conf. Ser.* **133** 012012
[40] Gudmundsson J T, Kimura T and Lieberman M A 1999 *Plasma Sources Sci. Technol.* **8** 22
[41] Guerra V, Sá P A and Loureiro J 2001 *J. Phys. D: Appl. Phys.* **34** 1745
[42] Guerra V and Loureiro J 1997 *Plasma Sources Sci. Technol.* **6** 373
[43] Pintassilgo C D, Kutasi K and Loureiro J 2007 *Plasma Sources Sci. Technol.* **16** S115
[44] Turner M M and Lieberman M A 1999 *Plasma Sources Sci. Technol.* **8** 313