Chemical sputtering as important etching mechanism in plasma sterilization

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Abstract

We study the inactivation mechanisms of bacteria or biomolecules in low pressure plasmas in the European project BIODECON (www.rub.de/biodecon). In these plasmas, the absorption of UV radiation is usually the most effective inactivation mechanism. However, the UV radiation cannot usually reach every pathogen, because these are stacked or incorporated in a matrix (e.g. blood). Therefore some etching mechanism has to be active, which removes biological material from the contaminated surface and exposes hence all pathogens to UV radiation. Oxygen containing low pressure plasmas are very effective in etching of biological material. It is usually believed, that atomic oxygen alone is responsible for this fast etching. However, we will show that oxygen atoms alone do not react with biological material and that a synergism between ions and atomic oxygen, so called chemical sputtering, plays the main role in etching. Results from the Ar/O$_2$ inductively coupled plasma and from particle beam experiment using quantified beams of argon ions and oxygen atoms will be shown and discussed.

Introduction

Sterilization is a key technology in the medical industry [1,2]. Many sterilization methods are known to be efficient such as heat treatment, gamma radiation or exposure to toxic chemicals (ozone, ethylene oxide or hydrogen peroxide). All these methods have in common that they impose a severe stress on the objects to be decontaminated: the wear of surgical instruments is significant and implants made from thermolabile polymers loose their mechanical integrity [3]. One technology that avoids these issues is plasma sterilization. In plasma, a source gas is dissociated and ionized and reactive species such as electrons, ions, atoms, radicals and UV photons are interacting with the biological system to be inactivated. In such a process, the object itself can stay at rather moderate temperatures since the dissociation of the precursor gas is initiated in the plasma state. It has been proven that plasma sterilization can be very efficient in inactivating bacteria or pathogenic biomolecules [4–6].

Plasmas containing molecular oxygen are usually very effective in inactivation and removal of biological material. We have studied the effect of Ar/O$_2$ inductively coupled plasma (10 Pa, 200W absorbed power) and argon ion and atomic oxygen particle beams (cf. Fig. 1) on biomolecules and model film (hydrogenated amorphous carbon) in order to understand the fundamental inactivation and etch mechanisms.

Figure 1. Schematic of the experimental setups: (a) inductively coupled plasma with a two stage differential pumped mass spectrometer; (b) particle beam experiment with three atom sources and one ion source.
Results and discussion

We have already shown, that oxygen atoms alone do not react with biological material and that a synergism between ions and atomic oxygen, so called chemical sputtering, plays the main role in etching [7,8]. Fig. 2 shows spores of *bacillus atrophaeus* untreated (a) and treated (b) for one hour with flux of Ar⁺ ions (flow $1.5 \times 10^{14}$ cm$^{-2}$s$^{-1}$, energy 200 eV) and oxygen atoms (flow $2.4 \times 10^{15}$ cm$^{-2}$s$^{-1}$). The spores are efficiently etched as indicated by their shrinking size and appearance of deep trenches and pores. This erosion is explained by the simultaneous impact of ions and oxygen molecules leading to the process of chemical sputtering. The surface is activated by ion impact, followed by reactions of atomic oxygen at newly created active sites. When only oxygen atoms are used, the spore shape and size do not change.

![Figure 2: SEM images of *bacillus atrophaeus* spores: a) untreated spores; b) spores treated simultaneously by argon ions and oxygen atoms.](image)

![Figure 3: The comparison of ion flux and atomic oxygen flux to the surface with the etch rate of hydrogenated amorphous carbon film.](image)

To check, whether synergism between oxygen atoms and ions is also effective in plasma, where the ion energies are well below 200 eV, the fluxes of ions and oxygen atoms to the surface have been measured by means of retarding field analyzer and mass spectrometer respectively. These fluxes are compared in Fig. 3 to etch rates of hydrogenated amorphous carbon film measured at the same position. It is clearly visible, that the etch rate is proportional to the ion flux to the surface, not to atomic oxygen flux, in agreement with the chemical sputtering mechanism. It should be noted, that the mean ion energy under our experimental conditions is only 10 eV, suggesting, that the Ar⁺/O chemical sputtering has no energy threshold.

Conclusions

Spores of *Bacillus atrophaeus* were exposed to beams of Ar⁺ ions, oxygen molecules and oxygen atoms. It is shown, that only the simultaneous impact of O atoms or O₂ molecules and of argon ions causes a very effective etching and perforation of the spore coat. This is due to the process of chemical sputtering, where O atoms interact with ion-induced defects at the spore surface leading to the formation of e.g. CO and CO₂ and thus to etching. This observation is directly supported in experiments using inductively coupled Ar/O₂ plasma. The maximum etch rate is reached if both the ion and the O atom fluxes to the surface are optimized simultaneously. The contribution of chemical sputtering to the efficiency of the plasma-induced inactivation of bacteria is of great importance for the development and validation of plasma sterilization techniques.

References