Investigations on Plasma-Biomolecules Interactions as Fundamental Process for Plasma Medicine

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Abstract. Investigations on plasma-biomolecules interactions have been carried out as fundamental process for plasma applications in medical science and biological treatments. In this study, plasma interactions with L-alanine which are amino acids: the building blocks of proteins have been investigated in terms of physical effects. Effect of ion and photon irradiation on degradation of L-alanine has been studied via x-ray photoelectron spectroscopy (XPS) analysis of chemical bonding states. The XPS results showed that the decrease in the -CH_3 bond, >$C(NH_2)COOH$ bond, and -COOH bond peaks of main component of the L-alanine with increasing ion energy, ion dose and photon energy. The L-alanine degraded by ions and photons with energy over 6eV.

1. Introduction

Plasma applications in medical science and biological treatments recently have shown remarkable progress with worldwide attentions [1-11]. Considering that biological molecules (biomolecules) such as DNA, amino acids and proteins, which are the building blocks of cells and organs in a hierarchy manner, are basically composed of organic chemical compounds, it is significantly essential to perform fundamental studies in molecular and/or atomic levels for understanding plasma interactions with biomolecules during exposure with plasmas, which contain ions, radicals, electrons and photons. In the plasma interactions with organic materials, it is of great importance to study fundamental processes involved in plasma exposure, which may contribute to modification and/or degradation of the organic materials in complex synergetic manners via ions, radicals, electrons and photons. In our previous works, plasma interactions with soft materials have been performed on the basis of surface analysis with x-ray photoelectron spectroscopy (XPS), in terms of physical and chemical interactions using plasmas sustained with low-inductance antenna (LIA) modules. [12-14] Based on these scientific knowledge, the preset study extends the investigations further on plasma interactions with amino acids, which are the building blocks of

proteins. Experimental results obtained from plasma exposures to amino acids will be presented in terms of physical and chemical effects via XPS analysis of chemical bonding states.

2. Experimental

The Experiments have been performed by the discharge chamber installed with a set of 8 units of LIA. The LIA units were mounted on the top flange of the discharge chamber and were coupled to a RF power generator at 13.56 MHz via a matching network. Each LIA unit was connected in parallel to the matching network. The LIA unit consists of a U-shaped antenna conductor (with a 80 mm height and a 70 mm width), which was fully covered with dielectric tubing for complete isolation from the plasma [12]. The chamber had a 500 mm inner diameter and a 200 mm height, which was connected to diffusion chamber made of stainless-steel vessel with a 500 mm inner diameter and a 400 mm height [15]. Kinetic energy distributions impinging onto the ground potential (ion energy at the sheath edge) from the plasmas were measured using a mass separated ion energy analyzer (Hiden, EQP500), which was mounted beside the substrate holder. The Ar plasma sustained at an RF power of 1000 W. Optical emission spectra in UV and VUV regions were measured with VUV monochrometer (McPHERSON, 234/302) mounted on sidewall of the chamber.

Ion energy distributions of the argon ions impinging to the ground potential through the sheath edge of the argon plasmas were measured using the mass-separated ion-energy analyzer (the spectra not shown). Peak values of ion energy distributions decreased from15 eV to 6 eV with increasing Ar pressure from 0.67 Pa to 26.6 Pa (15 eV at 0.67 Pa, 13 eV at 1.3 Pa, 9 eVat 6.5 Pa, 7 eVat 13 Pa,
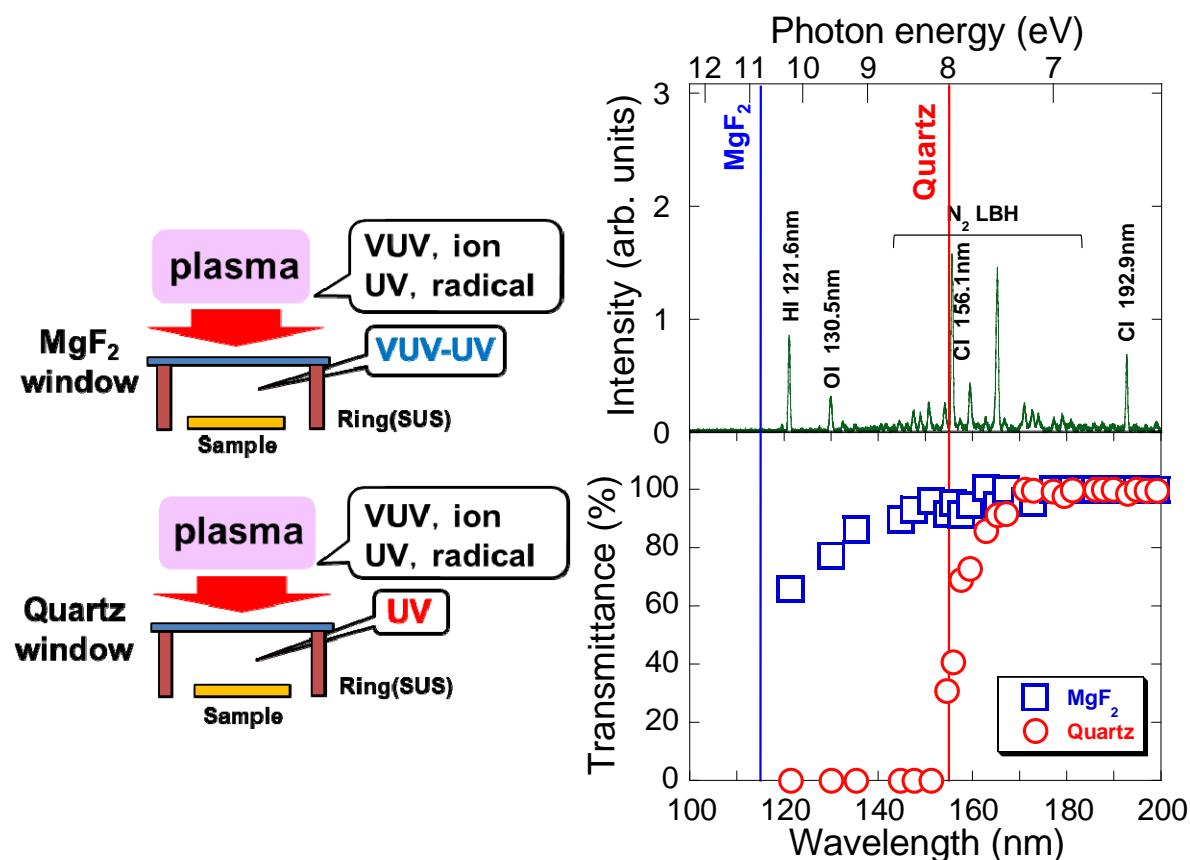

Figure 1. Schematic illustration of the apparatus used in photoirradiation and typical UV and VUV emission spectrum from the Ar plasma sustained at an RF power of 1000W together with the optical transmission properties of the MgF_2 and the quartz windows.

and 6 eVat 26 Pa) [17]. Furthermore, the ion-bombardment energy onto non-conductive substrate (the PET film in the present investigation) is almost equivalent to potential drop from plasma potential to floating potential. As reported in the previous work, the potential drop of argon plasma was in the range of 3–15 eV for Ar pressures of 0.26–13 Pa (15 eV at 0.26 Pa, 8 eV at 1.3 Pa, and 3 eV at 13 Pa) [17].

   For evaluating the interactions of the polymer surface with UV and VUV photons from the L-alanine were exposed to photons from the Ar plasmas by covering the L-alanine with MgF_2 and quartz windows as shown in Fig. 1. Here it is noted that thickness of the MgF_2 and quartz windows is 2 mm. The MgF_2 window is transparent in VUV+UV regions (wavelength longer than 115 nm corresponding to photon energy less than 11eV), whereas the quartz window is transparent in UV regions (wavelength longer than 155 nm corresponding to photon energy less than 8 eV). Therefore, it is possible to evaluate the effects of UV and VUV radiations by comparing results of the two samples with plasma exposed samples. [16]

   On the bases of these results for ion energy and optical emission, in this investigation, the chemical bonding states of L-alanine exposed to argon plasmas with a varying ion energy and photon energy were investigated.

   The analysis of chemical bonding states was carried out by x-ray photoelectron spectroscopy (XPS) (AXIS-165x SHIMADZU Corp., Japan). The XPS analysis was performed with non-monochromatized Mg Kα radiation (photon energy of 1253.6 eV).

3. Results

Figure 2 shows a typical XPS C 1s spectrum for the raw L-alanine together with chemical structure. The C 1s photoelectron spectrum from the L-alanine was composed of the following major components: $-CH_3$ bond peak at a binding energy of 285.4 eV, $>C(NH_2)COOH$ bond peak at 286.7 eV, and -COOH bond peak at 288.8 eV. [18]

   In order to investigate effect of ion irradiation on biomaterials, chemical bonding states of the L-alanine exposed to argon plasmas were examined by XPS. Figure 3 (a) shows XPS C 1s spectra of L-alanine exposed to argon plasma sustained at an RF power of 1000W and argon pressures of 0.67 Pa-26 Pa corresponding to ion energy range of 6 eV-15 eV with an ion dose of 4.3×10^{18} ions/cm^2. The spectra show the decrease in the $-CH_3$ bond, $>C(NH_2)COOH$ bond, and -COOH bond peaks of main component of the L-alanine. With increasing ion energy, the peaks of $>C(NH_2)COOH$ bond, and -
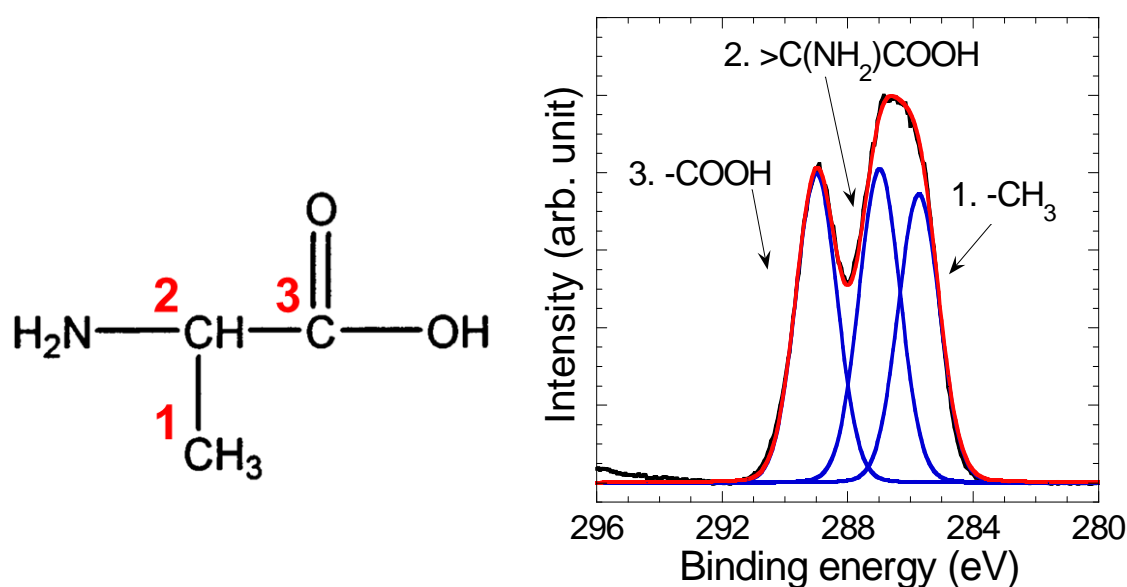

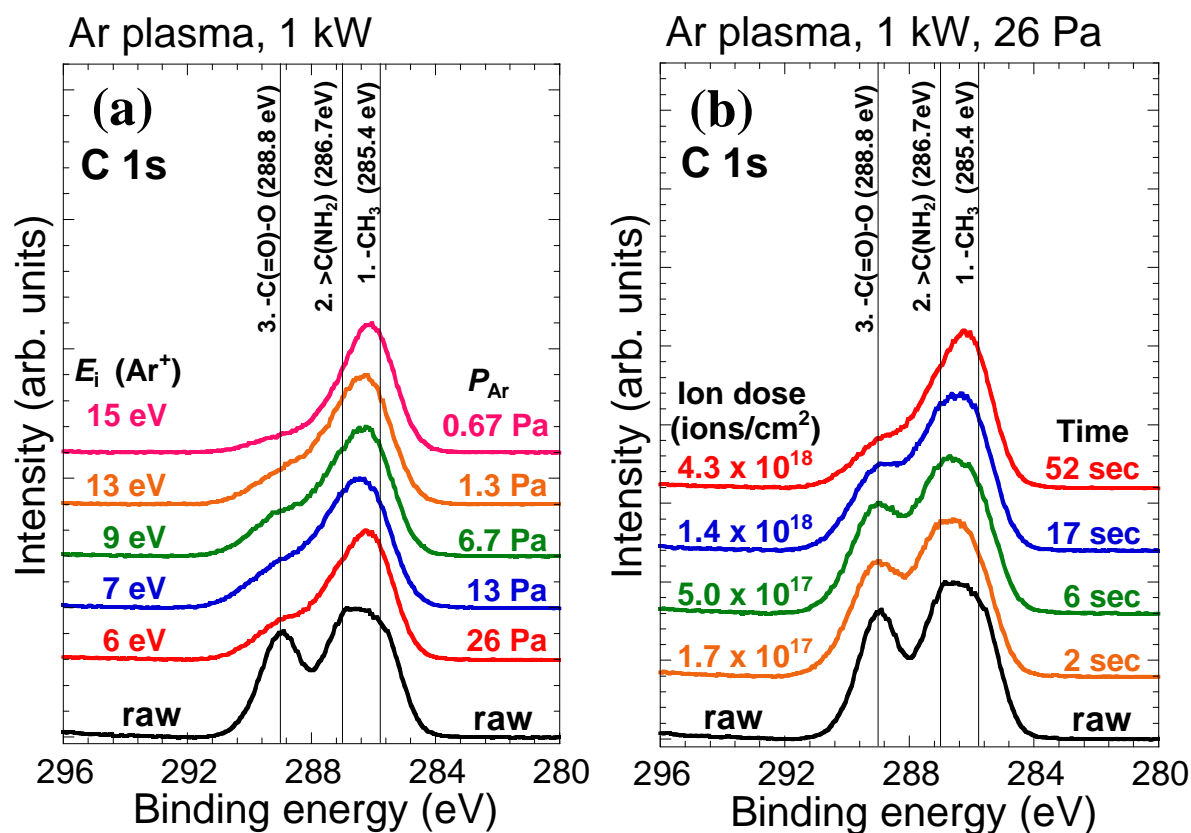**Figure 2.** Chemical structure and typical XPS C 1s spectrum of raw L-alanine.

Figure 3. The XPS C1s spectra for L-alanine without and with exposure to argon plasmas with a variation of argon pressures corresponding to ion bombardment energy and ion dose.

COOH bond drastically decreased. Figure 3 (b) shows XPS C 1s spectra of L-alanine exposed to argon plasma sustained at an RF power of 1000W and argon pressures of 26 Pa in an ion dose range of 1.7×10^{17} ions/cm^2 - 4.3×10^{18} ions/cm^2. With increasing ion dose, the peaks of >C(NH$_2$)COOH bond, and -COOH bond drastically decreased as is the case in the results of ion energy dependence. In the case with polymer materials including polyethylene terephthalate (PET), chemical bonding states of the PET films exposed to argon plasmas with ion energy of 6eV showed no degradation. [19] The results exhibit that L-alanine degraded at low energy compared with polymer materials including polyethylene terephthalate (PET).

Figure 4 shows the conventional XPS C1s spectra of L-alanine; (a) after direct exposure to the plasma, (b) after irradiation with the VUV+UV photons from the plasma (through the MgF$_2$ window), (c) after irradiation with the UV photons from the plasma (through the quartz window) (d) without photon irradiations (with only radials) and (d)before irradiation (raw). Here the spectra shown in Fig. 4 correspond to probing depth of about 10 nm from the surface. The samples after exposure to the Ar plasma and after the photoirradiation in the VUV+UV, the UV regions and without photon irradiations clearly exhibit significant decrease in the peaks of >C(NH$_2$)COOH bond, and -COOH bond. In particular, the XPS analyses show that the degradation of L-alanine after the photoirratiation in the UV + VUV regions as well as plasma irradiation is localized in the vicinity of the surface regions as shallow as 10 nm. Substantial degradation is found for the spectrum for irradiation of VUV+UV region corresponding to the spectrum for irradiation of UV region and without photon irradiations (with only radials). These results suggest that the photoirradiation in the VUV regions over 8eV may cause photodecomposition of the chemical bonds to create free radicals.
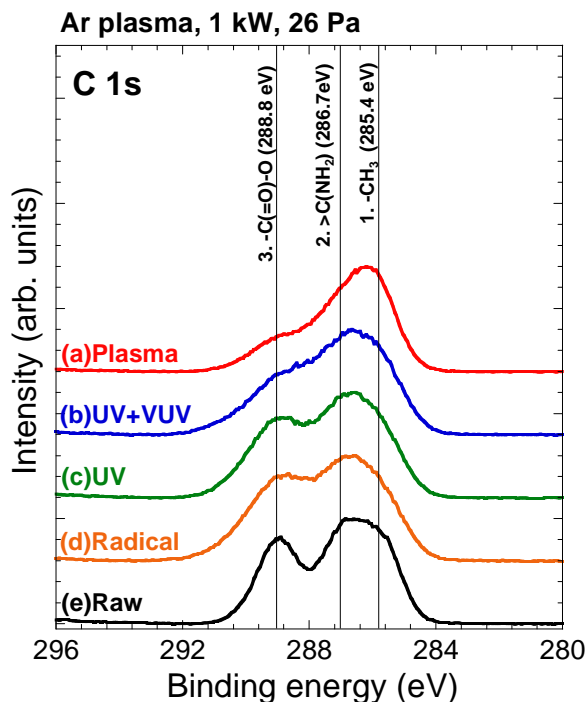
Figure 4. XPS C1s spectra for L-alanine; (a)after direct exposure to the Ar plasma, (b)after irradiation with the VUV+UV photons from the plasma (through the MgF_2 window), (c)after irradiation with the UV photons from the plasma (through the quartz window), (d)without photon irradiations (radical irradiation) and (e)before irradiation (raw).

These results for ion and photon irradiations exhibit that the degradation of L-alanine was occurred for low energy compared with polymer materials including polyethylene terephthalate (PET). It is considered that the degradation of L-alanine was occurred by direct fragmentation due to impinging of ions and photons since L-alanine is monomer.

4. Summary

Investigations on plasma-biomolecules interactions have been carried out as fundamental process for plasma applications in medical science and biological treatments. In this study, plasma interactions with L-alanine which are amino acids: the building blocks of proteins have been investigated in terms of physical effects. Effect of ion and photon irradiation on degradation of L-alanine has been studied via x-ray photoelectron spectroscopy (XPS) analysis of chemical bonding states. The XPS results showed that the decrease in the -CH_3 bond, >$C(NH_2)COOH$ bond, and -COOH bond peaks of main component of the L-alanine with increasing ion energy, ion dose and photon energy and the L-alanine degraded by ions with energy over 6eV and photons with energy over 8eV. It is considered that the degradation of L-alanine may be occurred by direct fragmentation of L-alanine due to impinging of ions and photons.

Acknowledgments

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