

# Induction of bioactivity on silicone elastomer by simultaneous irradiation of oxygen cluster and monomer ion beams

M. Kawashita<sup>a,\*</sup>, R. Araki<sup>b</sup>, G.H. Takaoka<sup>b</sup>

<sup>a</sup> Center for Research Strategy and Support, Tohoku University, 6-6-11-1306-1 Aramaki-Aoba, Aoba-ku, Sendai 980-8579, Japan

<sup>b</sup> Photonics and Electronics Science and Engineering Center, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

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## Abstract

Silicone elastomer substrates were irradiated with acceleration voltages ranging from 3 to 9 kV and doses ranging from  $1 \times 10^{14}$  to  $2.5 \times 10^{15}$  ions  $\text{cm}^{-2}$  by the simultaneous use of oxygen cluster and monomer ( $\text{O}_2$  CM) ion beams, and then soaking in  $\text{CaCl}_2$  solution. The apatite-forming ability of the substrates was examined using a metastable calcium phosphate solution that had 1.5 times the ion concentrations of normal simulated body fluid (1.5SBF). Silicon oxide clusters ( $\text{SiO}_x$ ) were formed at the silicone elastomer surfaces and the hydrophilicity of the substrates was remarkably improved by the irradiation. The irradiated silicone elastomer substrates formed apatite in 1.5SBF, whereas unirradiated ones did not. These results suggest that irradiation using  $\text{O}_2$  CM ion beams is effective for inducing an apatite-forming ability on silicone elastomer substrates.

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## 1. Introduction

Silicone elastomer has been widely used to make catheters [1], but infection often occurs owing to its poor biocompatibility [2–4]. It is believed that such infection can be suppressed by coating apatite onto the silicone elastomer surface, because apatite shows excellent biocompatibility [5]. Many attempts have been made to coat apatite onto a silicone surface. For example, Furuzono et al. prepared hydroxyapatite/silicone composite in which hydroxyapatite particles were covalently bonded onto the silicone surface [6], and reported its mechanical properties and biocompatibility [7]. Another approach to apatite coating of a silicone surface is surface modification to form specific functional groups effective for apatite nucleation in the body environment [8,9] and subsequent soaking in a metastable calcium phosphate solution supersaturated with respect to apatite such as simulated body fluid (SBF). So far, chemical sur-

face treatments such as soaking in sodium hydroxide aqueous solution [10], sol-gel modification [11] and modification with silane-coupling agent [12,13] have been reported. However, the surface modification is not so easy for chemically stable polymers. In this study, we focused on physical surface modification utilizing ion beams, especially cluster ion beams [14] since they can modify the surface of chemically stable polymers easily by controlling the incident energy of the ions.

Many attempts have been reported for the physical surface modification of silicone elastomer using a single (monomer) ion beam technique [15–23], but none of these employed cluster ion beams. The cluster is an aggregate of a few tens to several thousands of atoms or molecules, and constitutes a new phase of matter, with significantly different properties than those of solids, liquids and gases [24]. The effect of cluster ion impact on a solid surface is very different from the single ion effect. One feature of the cluster ion impact is the low-energy irradiation, and damage-free irradiation can be achieved by adjusting the incident energy of the cluster ion beam [14]. Meanwhile,

\* Corresponding author. Tel./fax: +81 22 795 3937.

E-mail address: [m-kawa@ecei.tohoku.ac.jp](mailto:m-kawa@ecei.tohoku.ac.jp) (M. Kawashita).

the monomer ion beams with high incident energy produce free radicals and bond scissions on the irradiated polymer surfaces that are effective for crosslinking and/or carbonization [25]. Recently, we investigated the apatite-forming ability of polyethylene (PE) substrates irradiated simultaneously by oxygen cluster and monomer ( $O_2$  CM) ion beams [26]. As a result, it was found that hydrophilic functional groups such as C–OH and/or COOH groups produced by the irradiation and the irradiated PE substrates formed apatite on their surfaces in a metastable calcium phosphate solution (1.5SBF) that had 1.5 times the ion concentrations of a normal SBF when they were previously treated with  $CaCl_2$  solution. On the other hand, Li et al. reported that silica gel with abundant Si–OH groups forms apatite on its surface in SBF, indicating the Si–OH group is effective for apatite formation [27]. On the basis of these findings, we can expect that the  $O_2$  CM ion beam is effective for the induction of an apatite-forming ability on silicone elastomer substrates as well as PE substrates. In this study, silicone elastomer substrates were irradiated with  $O_2$  CM ion beams with different acceleration voltages and doses, and the apatite-forming ability of the irradiated substrates in 1.5SBF is discussed in terms of the surface structural change due to the  $O_2$  CM ion beam irradiation.

## 2. Materials and methods

### 2.1. Simultaneous irradiation of $O_2$ CM ion beams

Details of the experimental apparatus for cluster ion beams have been given elsewhere [14]. Briefly, neutral beams of  $O_2$  clusters were produced by adiabatic expansion of a high-pressure gas through a glass nozzle into a high-vacuum chamber. In this study, we used  $O_2$  CM beams, since our previous study suggested  $O_2$  CM ion beams are more effective for surface modification of polymers than  $O_2$  cluster ion beams or  $O_2$  monomer ion beams [26,28]. The  $O_2$  CM ion beams were introduced into the ionization and irradiation chamber under an inlet gas pressure of  $4.0 \times 10^4$  Pa and ionized by electron bombardment with an ionization voltage of 300 V and an electron current of 300 mA. Silicone elastomer substrates  $20 \text{ mm} \times 20 \text{ mm} \times 1 \text{ mm}$  in size (AS ONE, Osaka, Japan) were irradiated at different doses ranging from  $1 \times 10^{14}$  to  $2.5 \times 10^{15}$  ions  $\text{cm}^{-2}$  by the simultaneous use of  $O_2$  CM ion beams. The acceleration voltage ( $V_a$ ) for the ion beams was changed from 3 to 9 kV.

### 2.2. Treatment in $CaCl_2$ aqueous solution and soaking in 1.5SBF

The substrates were soaked for 24 h at 42 °C in 120 ml of  $1 \text{ mol dm}^{-3}$   $CaCl_2$  aqueous solution to enhance apatite nucleation [29,30], and then immersed for 7 days in 120 ml of a metastable calcium phosphate solution (1.5SBF) that had 1.5 times the ion concentrations of a normal SBF [31–33]. In this study, the temperature of 1.5SBF

Table 1

Ion concentrations and pH values of human blood plasma, SBF and 1.5SBF

Ion	Ion concentration ( $\text{mmol/dm}^3$ )		
	Human blood plasma	SBF	1.5SBF
$Na^+$	142.0	142.0	213
$K^+$	5.0	5.0	7.5
$Mg^{2+}$	1.5	1.5	2.25
$Ca^{2+}$	2.5	2.5	3.75
$Cl^-$	103.0	148.8	222
$HCO_3^-$	27.0	4.2	6.3
$HPO_4^{2-}$	1.0	1.0	1.5
$SO_4^{2-}$	0.5	0.5	0.75
pH	7.2–7.4	7.4	7.4

was set at 42 °C to investigate the apatite-forming ability in a short period. The 1.5SBF was prepared by dissolving  $NaCl$ ,  $NaHCO_3$ ,  $KCl$ ,  $K_2HPO_4 \cdot 3H_2O$ ,  $MgCl_2 \cdot 6H_2O$ ,  $CaCl_2$  and  $Na_2SO_4$  (Nacalai Tesque, Kyoto Japan) in ultra-pure water, and buffering at pH 7.40 and 36.5 °C with tris(hydroxymethyl)aminomethane ( $(CH_2OH)_3CNH_2$ ) and  $1 \text{ mol dm}^{-3}$   $HCl$  aqueous solution (Nacalai Tesque, Kyoto, Japan). The ion concentrations and pH of human blood plasma, SBF and 1.5SBF are listed in Table 1.

### 2.3. Surface characterization

Surface structural changes to the substrates following irradiation by the  $O_2$  CM ion beams and 1.5SBF soaking were investigated with X-ray photoelectron spectroscopy (XPS; AXIS-165S, Shimadzu, Kyoto, Japan), thin-film X-ray diffractometry (TF-XRD; RINT-2500, Rigaku, Tokyo, Japan) and field emission scanning electron microscopy (FE-SEM; S-4500, Hitachi, Tokyo, Japan). The water contact angle of the substrates was measured with a contact angle meter (CA-D, Kyowa Interface Science, Saitama, Japan). Overlapping XPS peaks were separated into several peaks by a pattern-fitting method using the Gaussian profile for the individual peaks. In the fitting, the full width at half maximum was not fixed.

## 3. Results and discussion

Table 2 shows atomic concentrations of carbon, oxygen and silicon at the surfaces of silicone elastomer substrates

Table 2

Atomic concentrations of carbon, oxygen and silicon at the surface of silicone elastomer substrates unirradiated and irradiated by the simultaneous use of  $O_2$  CM ion beams at various acceleration voltages and doses

$V_a$ (kV)	Dose (ions/ $\text{cm}^2$ )	C (at.%)	O (at.%)	Si (at.%)
Unirradiated		51	24	25
3	$1 \times 10^{15}$	24	49	27
7	$1 \times 10^{15}$	29	49	21
9	$1 \times 10^{15}$	34	42	24
7	$1 \times 10^{14}$	41	34	25
7	$2.5 \times 10^{15}$	27	49	24

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