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Electron beam influence on the carbon contamination of electron irradiated hydroxyapatite thin films

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ABSTRACT

Electron beam irradiation which is considered a reliable method for tailoring the surface charge of hydroxyapatite is hindered by carbon contamination. Separating the effects of the carbon contamination from those of irradiation-induced trapped charge is important for a wide range of biological applications. In this work we focus on the understanding of the electron-beam-induced carbon contamination with special emphasis on the influence of the electron irradiation parameters on this phenomenon. Phase imaging in atomic force microscopy is used to evaluate the influence of electron energy, beam current and irradiation time on the shape and size of the resulted contamination patterns. Different processes involved in the carbon contamination of hydroxyapatite are discussed.

1. Introduction

Biocompatibility and structural properties that resemble those of hard tissues within the human body, such as bone and teeth, have promoted hydroxyapatite (HA) as one of the key biomaterials. HA is currently being used in a wide variety of biomedical applications [1,2], especially for dental and orthopedic implant coatings [3–5]. Biomaterial connected strategies for improving the biological response, tissue compatibility and adhesion of biological cells or biomolecules have gained massive interest in the last decade. Tailoring the surface properties is particularly desired as these were proven to influence the interaction of biomaterials with cells or tissues [6–8]. Among the surface properties which have been the target of research we can mention surface roughness, chemical composition and in particular surface potential. One of the recently proposed methods for surface potential modification is electron beam irradiation, by using either a low energy electron beam [9,10], or a high energy electron beam [11]. The latter method is of particular interest as it produces both negatively and positively charged micro-patterns without requiring to mask the targeted areas, as it is necessary in the case of the low energy method. In addition to the trapping of charge at irradiation-induced and/or pre-existing defects within the sample [10,12], electron beam irradiation of HA has been proven to induce a dissociation of residual hydrocarbons [13]. Hydrocarbon molecules can either originate from the oil pumping system or can be present on the specimen surface and specimen holder due to handling in the ambient. As a result of complex electron beam-induced reactions hydrocarbon molecules decompose and, depending on the beam diameter and the irradiation method [14], a carbon contamination pattern appears on the sample surface either in the shape of a carbon ring or of a pillar. Characterization of the carbon contamination distribution after electron beam irradiation has been performed in previous assays by using atomic force microscopy (AFM) [13,15], scanning Auger electron spectroscopy (AES) [16] and scanning electron microscopy (SEM) [17]. In one of our previous experiments based on multiple scanning probe microscopy techniques [18] we have used phase imaging in AFM and observed that it is a more reliable and faster method than the scanning AES for imaging carbon contamination patterns [19].

The work presented here had been focused toward gaining a better understanding of the carbon contamination that occurs after electron beam irradiation of HA surfaces. Special emphasis was placed on elucidating the influence that electron irradiation parameters such as electron energy, beam current and irradiation time have with respect to the shape and size of the contaminated areas. Because typically electron-beam-induced surface charge on HA is accompanied by surface carbon contamination, which is considered one of the physical mechanisms influencing the shape and size of these charge patterns [9], an evaluation of the effect of the electron energy on the surface potential patterning of HA [20] is not enough. It is thus important to identify the influence of

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different irradiation parameters on the carbon contamination layer, as this would enable separating the influence of the trapped charge on the bio/non-bio interaction from that of the carbon contamination. Elucidating such aspects would play a key role for optimizing a wide variety of biomedical applications based on HA.

2. Materials and methods

HA thin films were obtained by using a sol–gel method followed by spin-coating on silicon substrates and annealing. A 300 nm thick HA layer was obtained as determined in cross-section by SEM. Details about the fabrication procedure for the HA thin films can be found in a previous publication [11].

Electron beam irradiation of the HA sample was done in a SEM chamber with a stationary electron beam. The irradiations were made at accelerating voltages of 20 kV and 30 kV. The electron doses were controlled by varying the absorbed beam currents (1.4 nA and 14 nA) and beam irradiation times (7 s, 70 s, and 700 s). The initial electron beam diameter ranged from 350 nm for the lowest current to 850 nm for the highest current used. The pressure in the SEM chamber was kept at a value of 10^{-4} Pa during the experiments.

The structures resulted after carbon contamination were analyzed under ambient conditions using a Q-Scope 350 AFM (Quesant, USA). Tapping mode topographies and phase images were recorded by using Ti–Pt AFM probes with a nominal resonance frequency of 60 kHz, force constant 3 N/m and tip radius of curvature less then 35 nm. In AFM tapping mode, mapping the phase lag between the drive signal and actual probe oscillation generates an image known as AFM phase image which can be used to detect contaminants, variation in surface composition and regions with high or low surface adhesion or hardness [21,22].

The escape area diameters for the backscattered electrons (BSEs) were estimated by using the free CASINO software for Monte Carlo simulation of electron trajectories in solids [23]. The simulated sample consisted in a 300 nm thick HA layer with a density of 3.16 g/cm3 [24] deposited on a silicon substrate. Each time 10^6 electron trajectories were calculated and the BSEs escape areas were recorded.

3. Results and discussions

Typical carbon contamination patterns after electron beam irradiation of HA surface imaged by using AFM phase mode are shown in Fig. 1. AFM tapping mode images (Fig. 1, inset), illustrate that no surface topography modifications occur after the irradiation.

Previous X-ray photoelectron spectroscopy assays [11] performed on the irradiated areas ruled out electron-beam-induced chemical changes on the HA surface, as the Ca/P ratio which is a good indicator for the electron-induced damage [25] remained constant.

When incident beam electrons, also called primary electrons (PEs) hit a dielectric target covered with adsorbed hydrocarbon molecules, two processes should be taken into consideration.

First, the specimen charges electrically because PEs can be trapped at pre-existing and irradiation-induced defects within the sample and also because PEs scattering through the target produce secondary electrons (SEs), which eventually escape through the surface. Depending on the acceleration energy which controls the SE yield, the material becomes either positively or negatively charged. These excess positive or negative charges are accumulated in the specimen, causing a change in the electrostatic potential [26,27]. We have shown that in the case of electron irradiation of HA surface, with electron energies of 20 keV, surface domains with mainly negative charge are created [19]. The PEs also generates backscattered electrons, which can bounce further in the substrate and produce supplementary SEs.

The second important process consists in the formation of a carbon contamination layer. The contamination appears due to the interaction of SEs and BSEs emitted from the sample with hydrocarbon molecules present on the impact area or diffusing toward the beam impact point.

An important factor which influences the size and shape of the contamination area is the mechanism by which hydrocarbon molecules arrive at the electron impact point [28]: diffusion along the substrate from an unexposed region, or adsorption from the vacuum. Since the SEM chamber was kept at a pressure of 10^{-4} Pa during the experiments and the HA samples were not cleaned prior to the electron irradiation, we will consider hydrocarbons present on the sample surface as the main contamination source, hence diffusion at the surface being the mechanism by which they are supplied to the electron-exposed region.

In the case of a finely focused electron beam kept stationary on the target surface, in most cases, the shape of the carbon contamination deposit consists in two components [29]. One is a pillar situated at the beam impact point produced by PEs and the second component is a ring surrounding the central pillar formed by BSEs and SEs generated by BSEs interacting with the molecules present at the surface. The ring surrounding the central pillar has a diameter corresponding to the BSEs escape area.

In our case, all the contamination patterns are rings or disks (Fig. 1) which are created around the electron beam impact point, without the formation of the central pillar. Charging of the sample is accompanied by a charge spreading due to an induced radial field in the domain which increases with the distance from the central irradiation point [30]. This leads to a spreading of the PEs impact area and to an effective defocusing of the incident beam. According to Cazaux [30], the induced electric field will increase the concentration of molecules at the perimeter of the beam. This enhanced diffusion of hydrocarbon molecules to the periphery of the irradiated area, explains the formation of only a ring- or disk-shaped pattern and not the two-component domains presented earlier.

To aid the discussion, Fig. 2 shows the simulated BSEs escape area diameter evolution with the defocusing of the incident electron beam for two different electron energies. In both cases with the increase of the incident electron beam diameter, the BSEs escape area diameter increases. Because BSEs are responsible for the cross-linking of hydrocarbon molecules and formation of the carbon contamination layer, we can estimate that the carbon contamination diameter will increase for a defocused beam. In addition to the increase of the contamination area with the defocusing of the beam, the simulations provide an answer for the shape of the contamination domains. As the incident electron beam is more defocused, the BSEs escape area profiles change from disk-shaped to ring-shaped, a situation which is in agreement with the AFM experimental data (Fig. 1).

Formation of the ring carbon deposit can now be explained as resulting from the convolution of the BSEs distribution generated by a defocused irradiation electron beam and the concentration profile of the adsorbed hydrocarbon molecules established by surface diffusion at the electron impact point. Both components affecting the carbon contamination deposit are influenced by the electron-beam-induced surface charging as we have demonstrated earlier.

Going one step further with the analysis of the carbon contamination we investigated the influence of the electron energy, irradiation time and beam current on the carbon patterns. We first analyzed the effect of the electron energy (Fig. 3) and observed an increase in the external diameter (Table 1) explained by the increase of the BSEs escape area (Fig. 2a). In the same time one can observe an increase in the internal diameter with the incident