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Surface potential patterning of hydroxyapatite films by focused electron beam: Influence of the electron energy

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ABSTRACT

Surface potential (SP) of biomaterials surfaces is known to significantly influence adsorption of biological cells and biomolecules. Its modifications thus play an important role in biological and medical applications. In this work, focused electron beam typically available in scanning electron microscopes has been used to create micro-domains with modified SP on nano-crystalline hydroxyapatite thin films. The resulting SP distribution has been studied by the Kelvin probe force microscopy technique as a function of the incident electron energy in the range from 3 to 30 keV for varying beam current, i.e. speed of the charge injection. Factors limiting minimal size of such SP patterns are discusses.

1. Introduction

Development in the field of biomaterials and their biological response is important for many areas of medical applications. Modifications of biomaterial's surface properties are particularly aimed at controlling the surface adhesion and growth of biological cells and biomolecules such as proteins [1,2]. These properties are determined by several factors including the surface roughness, porosity, chemical composition and in particular the surface potential (SP) and wettability of the material [1]. Several methods for surface modification in terms of wettability and SP have been proposed. Among others, deposition of monolayers, application of external electric field [2], photon irradiation [3], plasma modification [3], ion beam [4] and recently electron irradiation [5–8] have been successfully used. The last mentioned method has several benefits: possibility of precise creation of desired SP patterns on micrometer scale with both positively and negatively altered SP and corresponding wettability modification and patterning in wide range of contact angles [6]. The SP of a material can significantly affect the promotion or reduction of adsorption of biological cells and biomolecules depending on their overall surface charge and its distribution [1,9,10]. On an example of Lysozyme it has been shown that the protein adsorption can be increased or suppressed several times by such SP modification [11,12]. The SP patterning can thus be used to regulate their distribution on a surface with high lateral resolution, what can be utilized e.g. in tissue engineering or biosensor applications as well as basic research tasks. In the ideal case, regulation of adsorption of individual cells or biomolecules can be achieved if the SP patterns are comparable with their size.

In this work we have focused on influence of the impact electron energy (3–30 keV) on the size of the SP patterns created by direct electron beam irradiation on hydroxyapatite (HAp) films. We show that for given setup and irradiation parameters, the size of the patterns is considerably energy dependant with minimum given mainly by the beam diameter and its interaction volume within the material. It is also shown that for given injected charge dose, smaller size of the patterns can be obtained by using smaller beam currents compensated by prolonging the irradiation time.

2. Experimental

The hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] thin films were prepared by a sol-gel method and subsequent spin-coating (4000 rpm for 50 s) on p-type (0 0 1) Si substrates. To prepare the sol–gel, phosphoric pentaoxide (P_2O_5) and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) were dissolved in pure ethanol to produce

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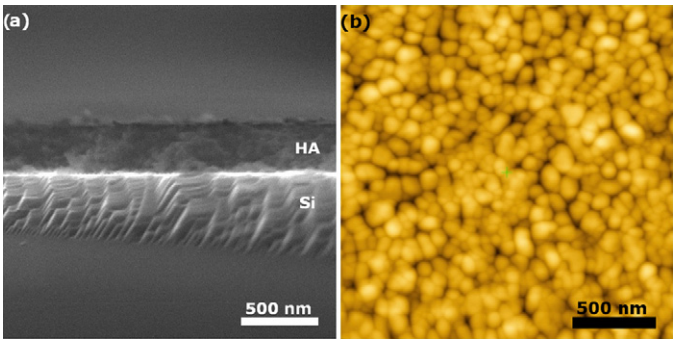

Fig. 1. (a) SEM cross-section micrograph of the HAp thin film. (b) AFM surface topography image of the HAp film (height scale is 35 nm).

solution with concentration of a 0.5 mol/l and a 1.67 mol/l, respectively. The precursor sol was prepared by mixing these two solutions proportionally to obtain a Ca/P molar ratio of 1.67. The mixture was continuously stirred at room temperature, and then heated to 70 °C for 1 h. Obtained transparent sol–gel was used for the deposition on Si substrates by spin-coating. After the deposition, the resulting films were aged at temperature of 100 °C for 30 min and subsequently calcined in air at 700 °C for 1 h.

Thickness of the HAp thin films has been measured in cross-section by a Scanning Electron Microscope (SEM) TESCAN VEGA II SBH. The electron-induced SP modification by the focused electron beam was done by SEM TESCAN VEGA TS 5136 MM with thermoemission cathode. A matrix of points on the HAp surface has been irradiated by the focused electron beam with the incident electron energy in the range from 3 to 30 keV. The absorbed electron beam current has been adjusted to 1.4, 14 or 100 nA for each energy on Co standard and than used with fixed beam parameters for the SP patterning of the HAp film. The irradiation times have been 70, 7 and 1 s, respectively, resulting in about ~100 nC injected charge for each point for all used currents. Although we are discussing the minimal size of the SP domains that can be obtained by such irradiation and smaller sizes are expected for lower currents and irradiation times, we have chosen relatively high doses for better comparison and increased manifestation of individual mechanisms influencing their creation.

The surface topography and SP of HAp thin films have been measured by Scanning Probe Microscope (SPM) NTegra Aura (NT-MDT Company). The surface topography images were obtained by semi-contact Atomic Force Microscopy (AFM) and the surface potential modifications have been studied by the Kelvin probe force microscopy (KPFM). Standard silicon AFM tips have been used for topography imaging only, while conductive TiN-coated AFM probes have been used for simultaneous AFM and KPFM imaging.

3. Results and discussion

The film thickness measured by SEM in cross-section was shown to be about 330 nm (Fig. 1a). Typical AFM surface topography image showing the nanocrystalline structure of the films is shown in Fig. 1b. Average surface roughness (S_a) of all samples determined by the AFM was less than 3 nm. Typical obtained SP patterns are shown in Fig. 2, while no surface topography modification was observed by AFM. For all used energies, circular domains of modified SP were observed. The SP distribution of the resulting domains is affected by many factors including the roughness, porosity, structural properties and thickness of the HAp thin film, the electron beam current and the time of irradiation [5] as well as the energy of the electron beam as can be clearly seen from Fig. 3. Physical mechanisms influencing the shape and size of the SP domains include: trapping of electrons and generated holes [6,8], emission of secondary electrons [13], surface contamination by carbon/hydrocarbon layer induced by the electron irradiation [6,14] and spreading of the charge carriers inside the material due to local electric fields [15,16]. Recently confirmed pyroelectric, and piezoelectric effects on unpoled HAp [17] suggest that polarization and/or depolarization effects may also play significant role. Chemical changes of the HAp induced by the electron beam (which could also affect the SP) were ruled out by X-ray photoelectron spectroscopy (XPS) measurements in our previous work [5], although some slight carbon/hydrocarbon contamination was observed.

Important factor, which is limiting some possible applications of this SP patterning approach, is the minimal possible size of the SP patterns which can be obtained. It is given by several factors. Except the motion of the charge carriers in the material and its surface, it is mostly limited by the electron beam diameter and the interaction volume of the electron beam inside the material. For given current, the beam diameter is increasing with decreasing electron energy as the slower electrons are harder to focus due to Coulomb repulsion. On the other hand, the interaction volume of the electron beam in the material is considerably increasing with increasing electron energy. The width w of this volume can be approximated by a simple empirical formula [18]:

$$w(\mu\mathrm{m}) = \frac{0.277E^{1,5}}{\rho} \quad (1)$$

where E (keV) is the impact electron energy and ρ (g/cm^3) is density of the irradiated material. Dependence of the electron beam diameter (calculated by the SEM software) in our experimental setup for used currents (1.4, 14 and 100 nA) and the width of the interaction

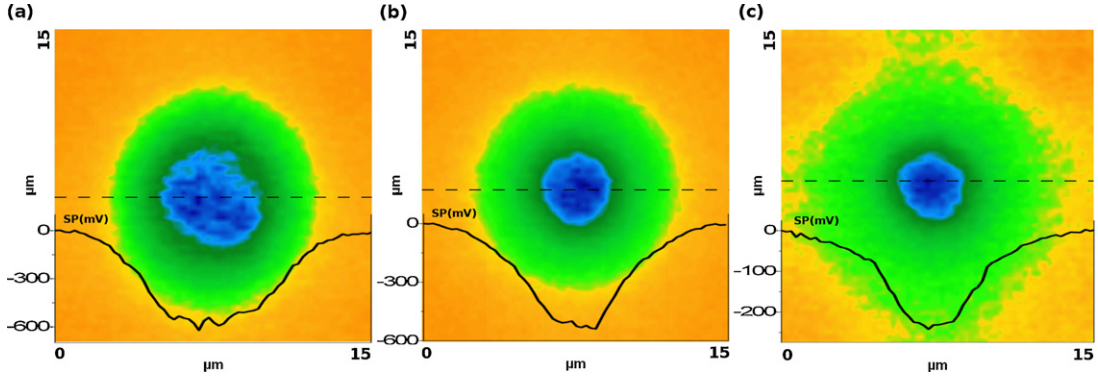

Fig. 2. SP distribution of the areas irradiated by focused electron beam with 100 nA beam current over 1 s with the incident electron energy (a) 10 keV; (b)20 keV; (c) 30 keV. Corresponding SP profile of cross-section indicated by dashed lines is shown under each image.