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Application of porous SiO_x layer as a template for calcium phosphate growth

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Calcium phosphate layers were grown on vacuum evaporated SiO_x layers by using a biomimetic approach (from an aqueous solution that resembles the ion compositions and concentrations in human blood plasma). Micro-Raman and Fourier transform infrared spectroscopy showed that the grown layer was calcium phosphate. Coherence probe microscopy revealed the formation of a white, inhomogeneous and rough layer with a peak-to-valley height and root mean square roughness of 16.4 and 5.4 μm, respectively. The layer reflection spectrum recorded by UV-Vis spectroscopy revealed low reflection and partial transparency in the visible region. From multiple-angle ellipsometric measurements at λ = 632.8 nm, a strong dependence of the refractive index and extinction coefficient on the angle of light incidence was established, due to density variations within the CaP layer.

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1. Introduction

Silicon (Si) is considered an essential element required by living organisms and a common constituent of biological minerals, together with Ca, P, Mg, Mn, Fe, S, C, O and H [1]. The widespread occurrence of siliceous biominerals as structural elements in lower plants and animals suggests a role for Si in the production and maintenance of connective tissue in higher organisms, although this function has not been clearly established [1].

Recently, a wide variety of porous and amorphous materials (porous Si, SiO_x, Ta, Ti, Al_2O_3, etc.) have been investigated as templates for biomedical applications [2,3]. The reason for such investigations is that porous structures allow fast deposition of biomaterial layers like apatite (a calcium phosphate phase - an inorganic component of bone and teeth), giving a strong surface adhesion and good osteointegration when implanted into a living body [3,4]. The calcium phosphate (CaP) layers grown on different templates by different methods contain nm-sized grains, and they can have significant porosity. The combination of nano-dimensions and porosity influences different biological events, and materials that possess such properties can be utilized in the laboratory to create biologically integrated multifunctional devices such as biomaterials and sensors [5,6].

In this work, we study the ability of a SiO_x layer to serve as a porous template for the growth of a nanostructured and porous CaP layer. The research approach undertaken for bioactivation of the SiO_x was immersion in an aqueous solution resembling the inorganic composition of the human blood plasma, and known as simulated body fluid (SBF) at physiological conditions of pH (7.4) and temperature (37 ^oC). This is known as the biomimetic approach, i.e. mimicking the physico-chemical conditions for mineral formation in nature.

2. Experimental

2.1. SiO_x growth

Thermal evaporation of SiO powder (Cerac 99.99%) on a Si substrate in vacuum ($2x10^{-3}$ Pa) was carried out. The SiO_x film was grown to a thickness of 630 nm. The angle of the SiO vapour stream to the Si substrate normal was 75^0, which yielded a porous SiO_x film with a columnar structure. The stoichiometric index of the amorphous SiO_x was x=1.5, rather high due to the promoted oxidation of thin oxide columns during evaporation in the residual oxygen atmosphere [7]. The content of cavities in this obliquely deposited SiO_x film was 66 % [7]. The columns and cavities were easily seen in the film surface by atomic force microscopic (AFM) imaging (Fig. 1). The rough surface, with a peak-to-peak S_y value of 13.8 nm and a root mean square roughness S_q of 1.94 nm, provides excellent conditions for the fast growth of biomaterial layers like apatite.

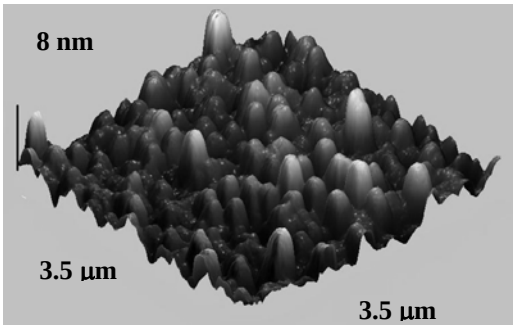

Fig. 1. 3D AFM surface image of the SiO_x layer

2.2. SBF preparation and CaP growth

SBF was prepared by dissolving reagent-grade chemicals (NaCl, $NaHCO_3$, KCl, K_2HPO_4-$3H_2O$, $MgCl_2$-$6H_2O$, $CaCl_2$-$2H_2O$, and Na_2SO_4-$10H_2O$) in distilled water and buffering at a pH of 7.4. The samples with the SiO_x layer were immersed in the SBF and left for 17 hours under physiological conditions (pH 7.4 and 37^0C).

2.3. Analysis

The topography of the grown CaP layers was observed by coherence probe microscopy (CPM), using a Leitz Linnik interferometer based system (λ = 350-1100 nm, dynamic range 100 μm, axial and lateral resolution of 10 nm and 0.45 μm, respectively). The layer structure was studied by micro-Raman spectroscopy (using a Renishaw Ramascope, λ = 488 nm, reflection mode). The layer reflection spectrum was recorded by UV-Vis spectroscopy (Perkin-Elmer, UV/Vis/NIR Spectrometer Lambda 19, spectral range 200-2500 nm). Additional information about the layer was obtained from ellipsometric measurements carried out at a wavelength of 632.8 nm and at incident angles of 45-50^o with a step of 2^o.

3. Results and discussion

A representative 3D image recorded by CPM of the layer grown after the immersion of the SiO_x template in the SBF is given in Fig. 2. It revealed the formation of a white and rough layer distributed over the whole surface of the underlying SiO_x. By measuring the surface line profiles, we estimated the layer peak-to-valley height and root mean square roughness to be 16.4 and 5.4 μm, respectively.

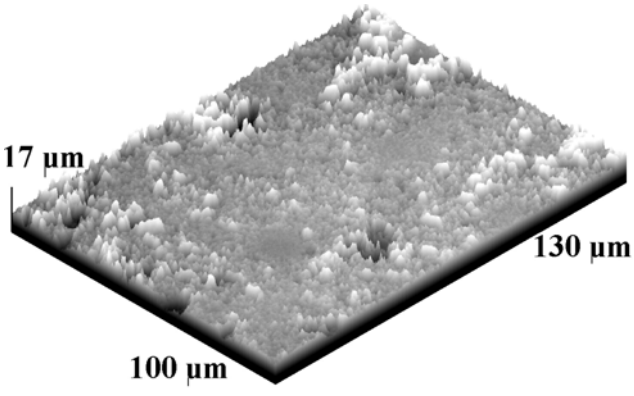

Fig. 2. 3D image of the CaP layer recorded by the CPM technique.

Micro-Raman spectroscopic investigation of the structure of the grown layer showed that it was CaP. As seen in Fig. 3a, the strongest P-O vibrational mode (v_1 symmetric stretching) of the PO_4^{3-} group, characteristic of CaP, appeared at 956 cm^{-1}. The low peak intensity and broad width was ascribed to a low degree of crystallinity and a nano-dimensional grain size. The intense peak appearing at 521 cm^{-1} is related to the first order Raman scattering of crystalline Si.

The reflection spectrum recorded by UV-Vis spectroscopy (Fig. 3b) additionally revealed low reflection of the CaP layer in the visible region. Raman and UV-Vis spectroscopy showed that the grown layer was partly transparent in the visible region.

The multiple angle ellipsometric measurements showed a strong dependence of the refractive index and extinction coefficient values on the angle of incident light (Fig. 4). This is evidence of density variations within the layer, most probably caused by inhomogeneously distributed cavities in the CaP layer. The dispersive effect of

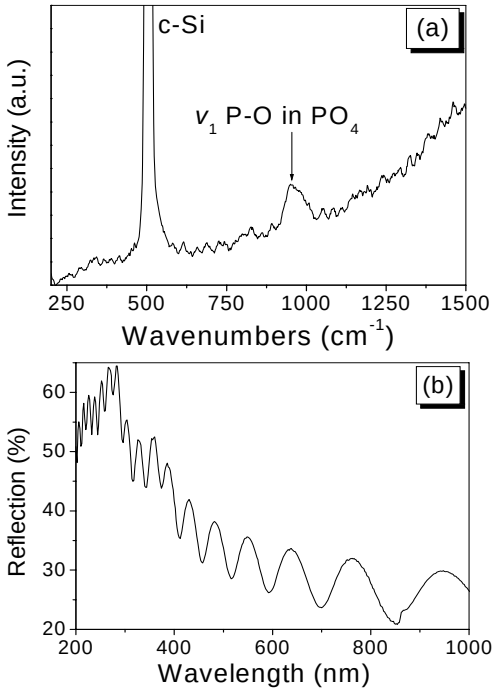

Fig. 3. Micro-Raman spectrum of the grown CaP layer (a); reflection spectrum of the CaP layer measured by UV-Vis spectroscopy (b).

the rough surface gives a significant contribution to the observed large values of the extinction coefficient. The ellipsometric results were supported by CPM observations, which actually revealed the presence of cavities within the volume of the CaP layer [8].

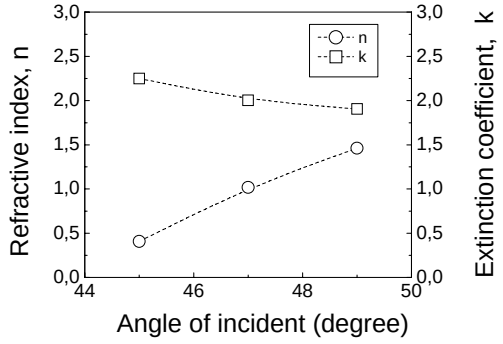

Fig. 4. Refractive index and extinction coefficient values as a function of the angle of light incidence.

4. Conclusions

It has been shown that a thermally evaporated porous SiO_x layer can serve as a template for the growth of a biomaterial layer through a biomimetic approach, forming a white, nanostructured and porous calcium phosphate layer distributed over the whole surface of the underlying SiO_x. To clarify the influence of the SiO_x template on the growth kinetics and layer properties, however, a more detailed study is needed.

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