BIOCERAMIC NANO-CALCIUM HYDROXYAPATITE COATINGS ON SILICON SUBTRATES

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Introduction

Bone is an organic-inorganic ceramic composite containing well-structured collagen fibrils, nanocrystalline, and rod-like inorganic material with length of 25–50 nm. Sequence of bone structure is formed from seven levels of hierarchy and reflects the material and mechanical properties of each component. Hydroxyapatite is chemically related to inorganic component of bone matrix as a complex structure with formula $Ca_{10}(OH)_2(PO_4)_6$ [1].

Applications of this material in various industries and medicine are investigated. Hydroxyapatite synthesized by different methods has different surface morphology and the products also have different chemical properties [2].

Experimental

Calcium hydroxyapatite coatings were formed on silicon substrates by sol-gel synthesis of calcium carbonate ($CaCO_3$) using two solutions:

No 1. In the sol-gel process, 1.8913 g of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) were dissolved in 20 ml of distilled water under continuous stirring at 80 °C. 0.5286 g of calcium acetate monohydrate ($Ca(CH_3COO)_2 \cdot H_2O$), 2 ml of 1,2-ethanediol ($C_2H_6O_2$) were added to the solution and mixed for 1 h. [3].

No 2. In the sol-gel process, 20 ml of 2-propanol were mixed with 1.8 ml of acetylacetone ($C_5H_8O_2$) with stirring at room temperature. An appropriate amount (1.0920 g) of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) was added to the solution and stirred for 1 h until the material dissolved [4].

The solutions used for coating the silicon substrates were mixed with the polyvinyl alcohol (PVA) solution in a ratio of 5:3. A polyvinyl alcohol (PVA) solution was obtained by dissolving 0.5 g of polyvinyl alcohol (PVA) in 49.5 ml of distilled water with stirring at 90 ° C for 1 h.

Silicon substrates were coated with 30 layers of each solution. Two silicon substrate coating techniques were used, which differ in the substrates rotational speed [Fig.1]. After each coating, the silicon substrate was heated in an oven at 200 °C for 10 minutes and in an oven at 600 °C for 5 hours at a rate of 5 degrees per minute. XRD, Raman spectroscopy, SEM analyses were performed after 10, 20, 30 coatings. Silicon substrates with surface-formed amorphous and crystalline calcium carbonate ($CaCO_3$) were stored in disodium hydrogen phosphate (Na_2HPO_4) solution for 28 days in a thermostat at 80 °C. XRD, Raman spectroscopy and SEM analysis was performed. The results of the analysis indicate the formation of hydroxyapatite in the coatings.

Results and discussion

Substrate coating technique a), sec	
RPM 1	1000
RAMP 1	1
TIME 1	1
RPM 2	3000
RAMP 2	2
TIME 2	1
RPM 3	3000
RAMP 3	1
TIME 3	30
RAMP 4	10

Substrate coating technique b), sec	
RPM 1	500
RAMP 1	2
TIME 1	5
RPM 2	1000
RAMP 2	2
TIME 2	5
RPM 3	1500
RAMP 3	2
TIME 3	90
RAMP 4	10

Fig. 1. Silicon substrate spin-coating techniques a) and b), which differ in the substrate rotational speed.

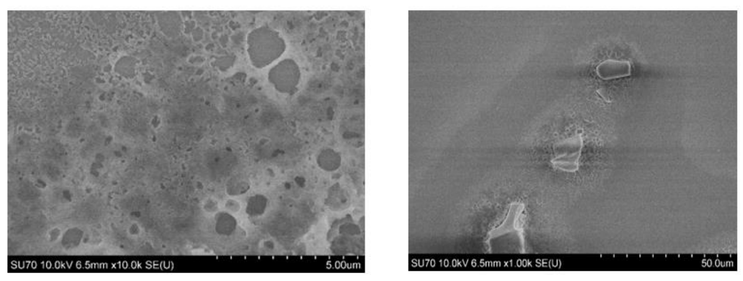

Fig. 2. SEM analysis shows single $CaCO_3$ crystallites are formed on silicon substrate using spin-coating technique.

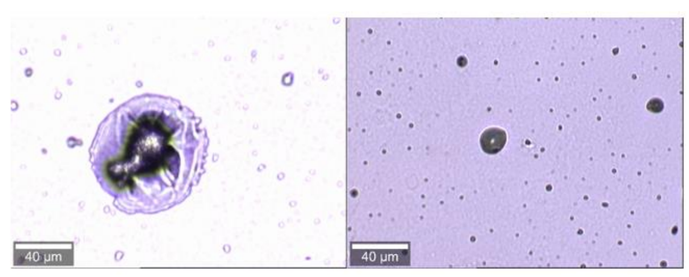

Fig. 3. Photographed on a Raman spectrometer. By pointing the laser at the individual crystallites formed, HA signals can be observed.

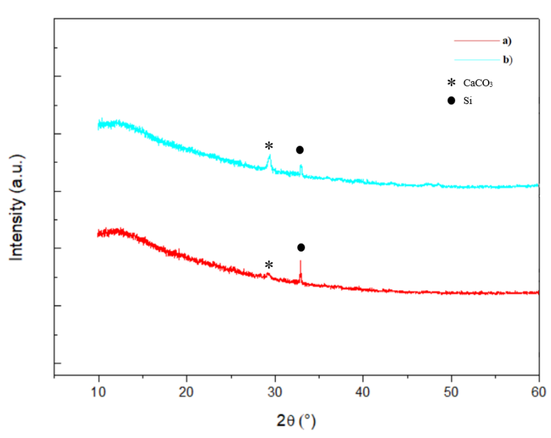

Fig. 4. XRD shows characteristic $CaCO_3$ peaks formed after 20 coatings using both spin-coating techniques a) and b).

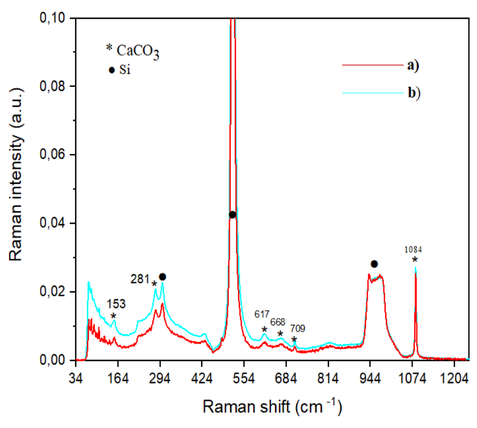

Fig. 5. Raman spectroscopy analysis shows characteristic $CaCO_3$ peaks at 153, 281, 617, 668, 709, 1084 cm^{-1} formed after 20 coatings using both spin-coating techniques a) and b).

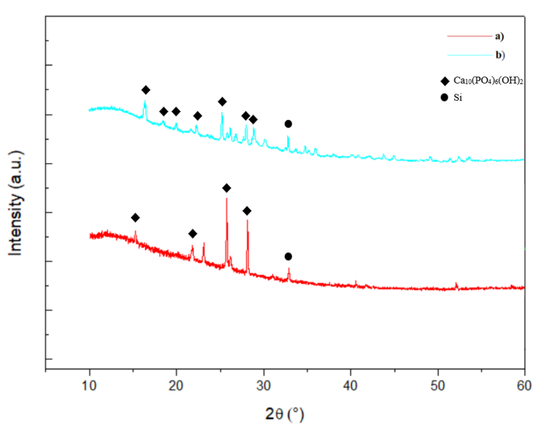

Fig. 6. XRD analysis shows characteristic HA peaks after Si substrates were stored in disodium hydrogen phosphate, Na_2HPO_4 solution (1 mol/l) for 28 days in a thermostat at 80 °C, using both spin-coating techniques.

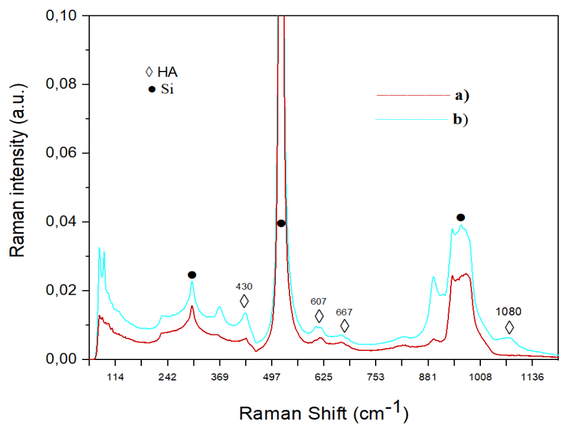

Fig. 7. Raman spectroscopy analysis shows characteristic HA peaks at 430, 607, 667, 1080 cm^{-1} formed after Si substrates were stored in disodium hydrogen phosphate, Na_2HPO_4 solution (1 mol/l) for 28 days in a thermostat at 80 °C, using both spin-coating techniques a) and b).

Conclusion

- Calcium hydroxyapatite coating formed on silicon substrates by sol-gel synthesis of calcium carbonate ($CaCO_3$) using solution No. 1 did not show good results, so all attention is paid to the analysis of coatings from solution No. 2.
- A new sol-gel method for the preparation of calcium hydroxyapatite thin films on silicon substrate using spin-coating technique has been developed.
- There is no differences between silicon substrate coating techniques a) and b), which only differ in the substrate rotational speed.
- The results of XRD and Raman spectroscopy led to the conclusion that with increasing amounts of coatings up to 30, the characteristic signal of HA material does not change. The optimum number of layers is 20. The results of the analysis indicate the formation of hydroxyapatite in the coatings.

References

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