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Production of thin film silicon-doped hydroxyapatite via sputter deposition

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Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ is used in a range of medical applications including coatings for hip replacements and bone grafting materials. However, relative to other bioactive glasses and glass ceramics, a longer time period is required for significant bone apposition to occur on the surface of phase pure HA implants, which increases patient rehabilitation time. An *in vivo* study by Patel *et al*. [1], compared bone apposition to sintered phase pure HA and silicon substituted HA ceramic implants, made by a precipitation reaction between calcium hydroxide and orthophosphoric acid, using silicon acetate as a source of silicate ions, demonstrating that bone apposition was significantly increased at the surface of silicon substituted HA ceramics. Thus, silicon addition could potentially accelerate the rate of fixation of the implant to the surrounding bone and improve the quality of implant performance [2].

It is essential when manufacturing HA by precipitation from solution that a Ca/P or Ca/(P + Si) ratio of 1.67 is achieved as otherwise secondary phases, such as tricalcium phosphate (TCP) can occur, which affect the bioactivity of HA [2]. At present, to maintain this ratio, it is only possible to incorporate a relatively low content of Si (3 wt% or 1.2 at.%) into the HA lattice structure using this technique [3].

Plasma-spraying is commercially the most frequently used method for deposition of calcium phosphate coatings, such as HA, onto implant materials to improve their bioactivity. However, despite clinical success, it has been recognized that the plasma-spraying method has several disadvantages, including poor long-term adherence of the coating to the substrate material, non-uniformity in thickness of the deposited layer, and variations in crystallinity and composition of the coating. As an alternative approach, sputter deposition has been employed as a successful coating technique for the deposition of calcium phosphate coatings [4].

The objective of this study was to deposit phase pure crystalline thin films of HA and silicon-doped HA (SiHA) with controlled compositions onto glass and Ti substrates by sputter deposition.

A 35 mm × 55 mm × 2 mm HA target block was slip-cast and then sintered at 1300 °C for two and a half hours. The sintered sputtering target was confirmed to be phase pure by X-ray diffraction (XRD) analysis. Pure HA films were deposited from this target using RF magnetron sputter deposition: the HA block was secured to a water-cooled magnetron body using spring clips. A similarly sized 99.999% pure Si sputtering target (Goodfellow Cambridge Ltd.) was employed for SiHA production, mounted on a second (DC) magnetron. All film deposition was performed in pure argon at a pressure of 0.85 Pa.

The target-substrate distance during deposition of pure HA films was 40 mm. The deposition rate was approximately 0.85 nm/min at a RF target power of 40 W. Films were subsequently heat treated in air at 500, 600 and 700 °C for 2 h. Film thickness was determined by masking a portion of a silicon substrate with a layer of Al foil, performing the deposition, and then removing the foil to leave a step in the film. The height of this step, and hence the thickness of the film, was then measured by profilometry. Deposited film thickness varied between 100 and 150 nm.

Thin film SiHA was deposited by cosputtering from two targets, as shown in Fig. 1. The HA and Si targets were positioned 45 mm above the substrate support, with a separation between the two targets of 100 mm.

TABLE I Relative positions of titanium (Ti) substrates during SiHA sputter deposition and resulting film composition

Distance to HA target (mm)	Distance to Si target (mm)	Sample	Composition (at.%Si)
45	130	Ti1	11.45
	140	Ti2	4.84
		Ti3	–
	150	Ti4	–
		Ti5	2.12
	160	Ti6	1.95
		Ti7	–

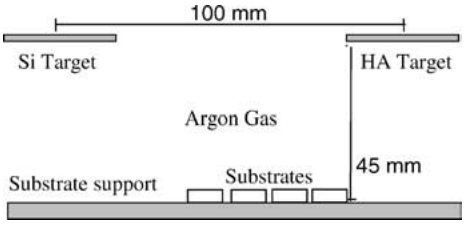

Figure 1 Setup for thin film SiHA sputter deposition.

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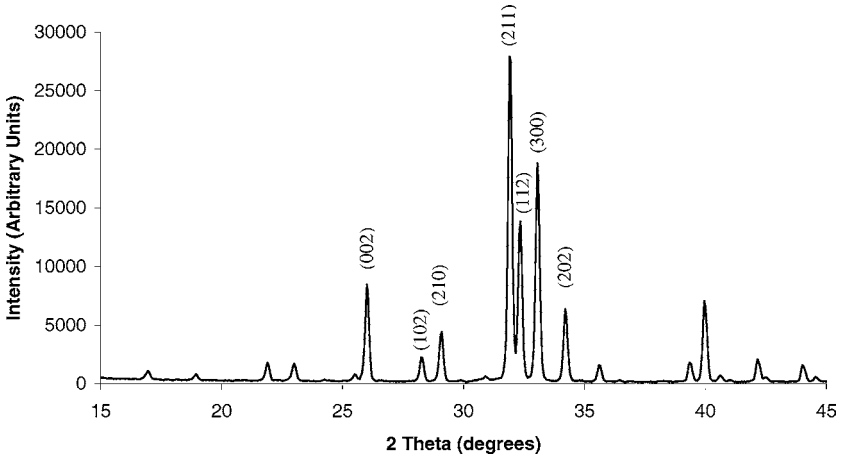


Figure 2 XRD trace showing phase purity of the HA target material.

The (dc) power to the Si target was 2.5 W. Because of the low HA deposition rate, substrates were placed underneath the HA target, and the Si content varied due to the differing Si target-substrate distance.

In a preliminary investigation, thin films of SiHA were deposited onto glass substrates. The position of these substrates was 130 mm from the silicon target. After film deposition, the substrates were heated in air at 600 °C for 2 h. Thin films of SiHA were then deposited onto titanium. The relative positions of the substrates are listed in Table I. After film deposition, the substrates were heated at 600 °C for 3 h.

XRD of the thin films was performed before and after heat treatment using a Phillips D500 diffractometer with Cu K_α radiation and with the X-ray generator operated at 40 kV and 40 mA. For the pure HA, data were collected with a step size of 0.05 ° and a dwell time of 40 s. For the SiHA, data were collected with a step size of 0.02 ° and a dwell time of 7.5 s was used. The slit sizes used were 1 ° divergence, 0.15 ° receiving and 1 ° antiscatter. Identification of the phases was achieved by comparing the diffraction patterns of HA and Si-HA with ICDD (JCPDS) standards [For HA, PDF Card no. 9-432 ICDD, Newton Square, Pennsylvania, USA].

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were performed using a JSM-5800LV SEM operated at 8 kV. Additionally, one SiHA sample in a position closest to the silicon target; (see Table I) was deposited on a lacy carbon film, nickel TEM grid (Agar Scientific, Essex, UK) and was observed before and after annealing in a Philips CM30 transmission electron microscope (TEM) operated at 200 kV.

The phase purity of the HA target material was confirmed by XRD (Fig. 2). All as-sputtered HA and SiHA films showed amorphous XRD patterns and all films were crystalline after heat treatment (Figs 3–5).

XRD analysis of pure HA thin films on glass substrates annealed at 500, 600 and 700 °C (Fig. 3a–c) showed that all peaks obtained matched those for the HA standard. The intensity of the peaks varied at the

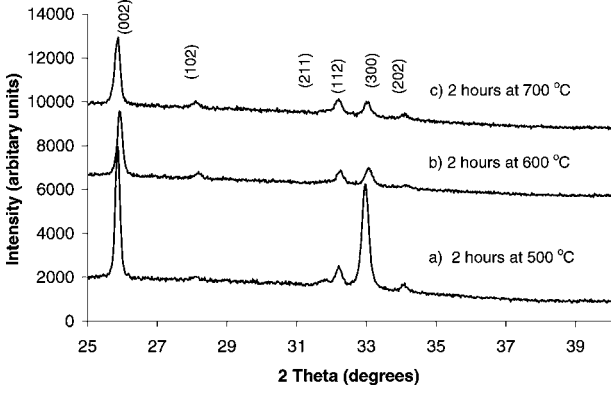


Figure 3 XRD traces of thin film pure HA, annealed for 2 h at: (a) 500 °C, (b) 600 °C, and (c) 700 °C.

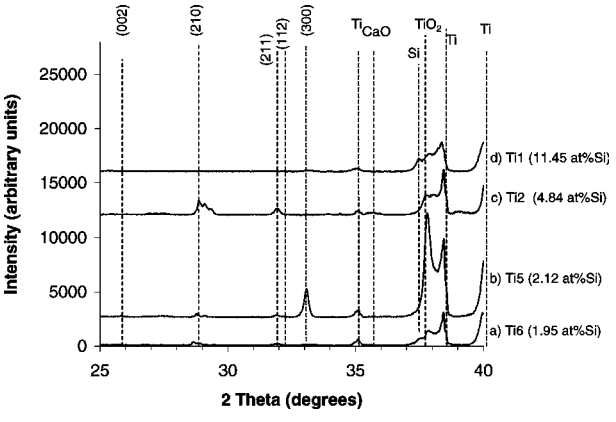


Figure 4 XRD traces of thin film SiHA on titanium substrates, annealed for 3 h at 600 °C: (a) Ti5, (b) Ti1, and (c) Ti7, (d) Ti2 (see Table I).

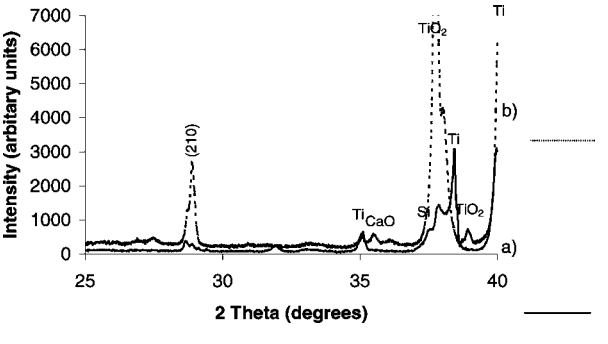
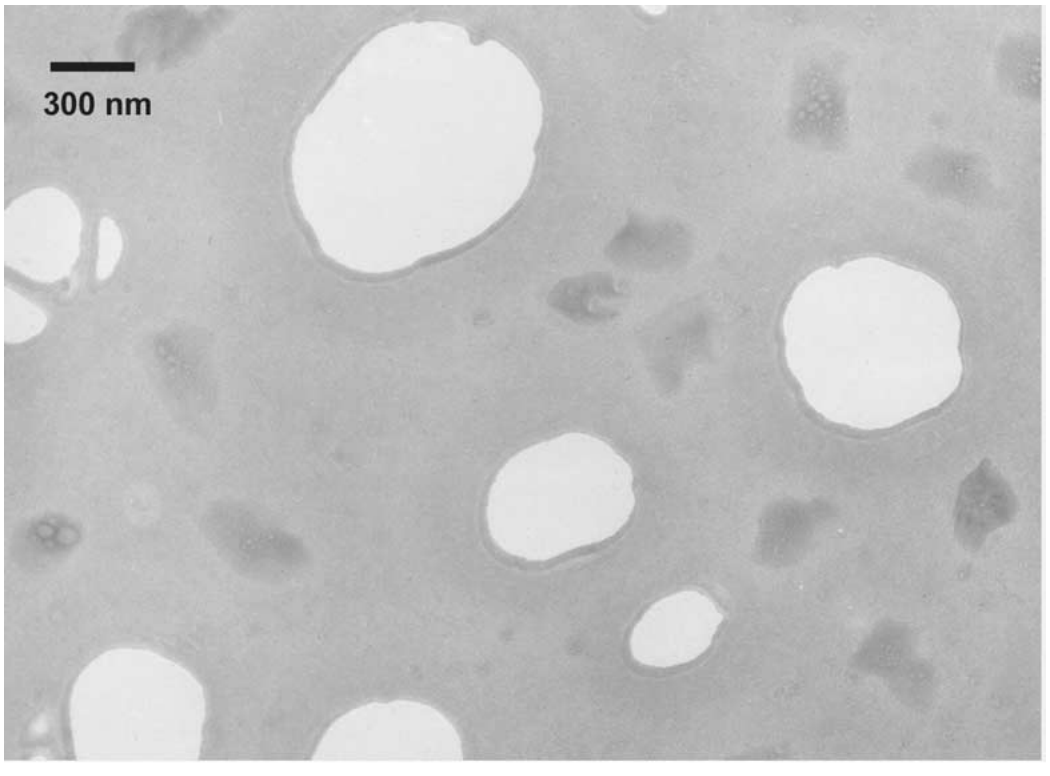


Figure 5 Effect of heat-treatment time on texture and crystallinity of thin film Si-HA on titanium substrates: (a) Ti7 heat-treated for 3 h at 600 °C and (b) Ti7 heat-treated for 24 h at 600 °C.

TABLE II Summary of EDX results for thin film Si-HA before and after heat-treatment. See Table I for sample identification

	Before heat treatment				After heat treatment (3 h, 600 °C)			
Sample	at.% Ca	at.% P	at.% Si	Ca:(Si + P)	at.% Ca	at.% P	at.% Si	Ca:(Si + P)
Ti1	19.98	6.46	6.62	1.53	18.59	3.75	11.35	1.23
Ti2	22.17	7.94	3.18	2.00	21.16	6.73	4.84	1.83
Ti5	21.44	9.04	2.17	1.91	20.65	9.20	2.12	1.82
Ti6	22.95	8.17	2.15	2.23	21.68	8.29	1.95	2.12



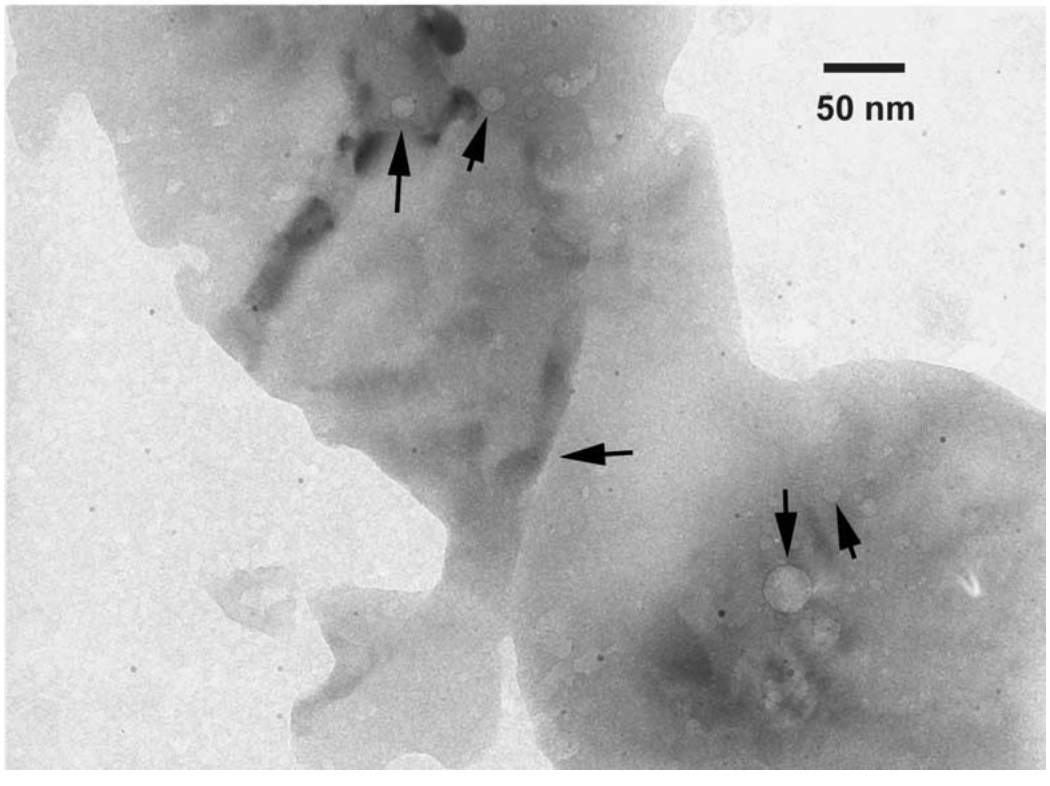


Figure 6 (a) TEM micrograph of SiHA crystallites. (b) TEM micrograph of SiHA illustrating the presence of grain boundaries and voids.

different annealing temperatures. The intensity of the (300) peak was significantly greater on the HA thin film heat-treated at 500 °C than on the films heat-treated at 600 or 700 °C.

Prior to heat treatment, SEM confirmed that the films were smooth and uniform, but afterwards some cracking was observed. EDX analysis data are displayed in Table II, and illustrate the variation in Si content, as well as changes in Ca/(P + Si) ratio upon heat treatment.

Crystalline HA XRD peaks (002), (210), (211) and (300) appeared in SiHA films deposited on glass and Ti substrates after heat-treatment (Fig. 4a–c). An additional CaO peak appeared on Ti2 (4.84 at % Si) at $2\theta = 35.6°$. At Si levels above 2.12 at. %, the intensity of HA peaks was lower (Fig. 4c and d) and sample Ti1 (11.45 at. % Si) included a silicon peak at 37.5 °. Interestingly, the (002), (112) and (202) peaks were absent on all Si-HA films but were present on thin films of HA. Additionally, the intensities of the HA peaks varied as the silicon content was increased. These findings imply that the silicon causes some texturing of the films. After continued heat-treatment (24 h at 600 °C) for Ti1 (11 at. %) Si (Fig. 5b) a CaO peak appeared. Additional peaks can be attributed to the titanium substrate ($2\theta = 35.02°$ and 38.42 °) and the formation of titanium oxide ($2\theta = 37.86°$) [Anatase 21-1272] (this was confirmed by checking the XRD patterns for heat-treated titanium substrates).

Transmission electron microscopy of a SiHA film with 6.7 at. % Si content after heat treatment revealed the presence of crystallites (Fig. 6a). Grain boundaries and voids were observed in many of the crystallites (Fig. 6b). Selected area electron diffraction (SAED) revealed crystalline spots and indexing of the spots confirmed the crystal lattice to be HA. EDX confirmed the presence of Ca, P and Si with a Ca/(P + Si) ratio of 1.71.

In conclusion, we have successfully illustrated the deposition of phase pure thin film HA and Si-doped HA by RF sputter deposition. Crystalline HA peaks were formed after heat-treating the films. Although the annealing temperature did not appear to affect the phase purity of the films it did have an effect on the relative intensities of the peaks in the XRD patterns. The intensity of the peaks, in particular of the (300) peak, on HA films heat-treated at 500 °C (for two hours) was more intense than on the HA heat-treated at 600 and 700 °C suggesting that initial crystal nucleation and growth occurs along the a-axis of the apatite crystals. We have also demonstrated that we can produce significantly thinner (100–150 nm) films than coatings produced via plasma-spraying (typically 30–200 μm). These findings illustrate the potential of RF magnetron sputter deposition as an attractive alternative technique to plasma-spraying, for depositing thin films of phase pure stoichiometric HA and Si-doped HA.

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