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Page No	Queries	Author Response
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## Chapter 28

Hydroxyapatite Thick Films  
as Pressure Sensors

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Electrical properties of hydroxyapatite (HA) in the form of screen-printed thick films that can be used as a biocompatible coating for bone and dental implants are reported. In particular, piezo- and pyroelectric behaviour of these films suggest that they can be used to promote faster healing of bones and prevent rejection of implants. Moreover, the reversible pressure-induced changes in their electrical characteristics can be employed for real-time *in vivo* pressure sensors implantable simultaneously, for example, with knee or hip prosthesis. The additional advantage of HA in the form of screen-printed thick films is that, due to the technology's versatility, it can be produced on flexible substrate in any shape and size to suit the needs of various patients.

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## 1. Introduction

Hydroxyapatite (HA) is a bioactive material with the ability to support bone growth. HA coated implants have been largely used in implants with bioactive fixation that rely on direct chemical bonding of the bone-implant interface.<sup>1,2</sup> It has high compressive strength but low flexural strength and fracture toughness. Due to the fact that HA does not exhibit good mechanical strength, it is often used as a coating material for different metal substrates. In this approach porous HA provides biocompatibility and space for bone ingrowth, while the metal substrate provides load bearing functions. HA coated implants are used in dentistry and orthopaedics due to their superior bonding with the host bone, achieved by bone ingrowth into the porous structure of HA coating. Polarisation of HA thick film and its effects on bone growth has been discussed in Chapter 9. In this chapter we report electrical properties of HA in the form of screen-printed thick films. Following the discussion of a theory behind pressure sensing, this chapter critically reviews the benefits of applying HA coatings on bone and dental implants. It then summarises the modern coating deposition techniques that are suitable for the biomedical industry, focusing on a special case of thick-film screen printing method, which was used to produce the bespoke pressure-sensitive HA coatings reported here. These can potentially be used as both the functional HA coating of any change and a real-time pressure sensor for implant performance monitoring.

## 2. Pressure Sensing Principles

The behaviour of screen printed HA thick films closely approximates the nature of standard capacitors. Since the tested HA samples can be treated as parallel-plate capacitors, pressure induced changes of capacitance can be explained simply. Application of pressure reduces the thickness of HA dielectric layer. Dependence of capacitance on the changes in the thickness can be described by

$$C = \varepsilon_0 \varepsilon_r \left( \frac{A}{d + \Delta d} \right) \quad (1)$$

1 where  $C$  is the capacitance,  $A$  is the area of plates, which was  
2  $3.17 \cdot 10^{-5} \text{ m}^2$  in this set of experiments,  $d$  is the thickness of the  
3 dielectric material and  $\Delta d$  is the change in the thickness due to  
4 applied pressure; while  $\epsilon_0$  and  $\epsilon_r$  represent the permittivity of free  
5 space and the dielectric material respectively.

### 6 **3. Printed Pressure Sensors in Medical Applications**

7 Medical technology is one of the most challenging markets for elec-  
8 tronics. Very high demands are placed on the precision, reliability and  
9 long-term stability of electronic systems. The same also applies to the  
10 electronic components and sensors. A wide range of pressure sensor  
11 dye, pressure transducers and pressure transmitters are available for  
12 pressure measurement in the most diverse medical applications, rang-  
13 ing from basic blood pressure sensors to ingestible microsensors for  
14 *in vivo* gastrointestinal tract pressure measurements.

15 Probably the most effective material for pressure sensing appli-  
16 cation is lead zirconate titanate (PZT). It has excellent piezoelectric  
17 properties, however due to existence of a lead phase its utilisation  
18 in biomedical applications is limited. The novelty of the approach  
19 reported in this chapter is that the HA coating acts as both the pro-  
20 moter of bone-implant ingrowth and as a sensor that monitors this  
21 process by real-time assessment of a load experienced by that very  
22 coating.

### 23 **4. Deposition Techniques of HA Coatings**

24 New technologies, such as electron beam evaporation, provide for  
25 creation of complex interface structures to enhance bone ingrowth  
26 in cement-free implants. For example, in specimens with a simulated  
27 HA coating, a bone ingrowth depth of  $500 \mu\text{m}$  yields substantial  
28 interface strength, whereas for the uncoated specimens a plateau  
29 was reached at  $1500 \mu\text{m}$  of ingrowth depth, and deeper ingrowth did  
30 not enhance the interface strength considerably.<sup>3</sup> This confirms that  
31 the HA-implant interface itself provides the main support matrix,  
32 while the depth of in-bone ingrowth does not always enhance the  
33 bone-implant interface strength.

1 There is a broad range of technologies to produce HA coatings  
2 depending on the type and location of implants, with bone and dental  
3 implants being the main example. The main methods of HA  
4 coatings and issues associated with them in medical applications  
5 are briefly reviewed in the following section. Thermal spraying techniques  
6 of HA have been long and widely established in the research  
7 community. Other most commonly used techniques include High  
8 Velocity Oxy-Fuel (HVOF), high velocity suspension flame spraying  
9 (HVSFS), chemical vapour deposition (CVD), physical vapour deposition  
10 (PVD), and electrophoretic deposition (EPD). The following  
11 sections will focus on these techniques and will describe them in more  
12 detail. Another novel technique, CoBlast<sup>TM</sup>, will also be discussed.

#### 13 4.1. HA coatings for bone and dental implants

14 HA coated implants have been used in dentistry and orthopaedics  
15 since the 1980s due to superior bonding between the host bone and  
16 HA coated implants that can be achieved by bone ingrowth into  
17 porous structure. HA coated implants reduce the risk of osteolysis  
18 and subsequent implant failure.

19 However, there are still concerns related to long-term *in vivo*  
20 stability of HA coated implants, although there is more evidence.<sup>4</sup>  
21 that porous HA coated acetabular components significantly enhanced  
22 bone in-growth in the presence of wear particles, preventing their  
23 migration and reducing osteolysis. Since HA particles are biodegradable  
24 and do not produce any inflammatory reaction in the surrounding  
25 bone, fears of osteolysis or third body wear due to HA debris  
26 have not been confirmed.<sup>5</sup> Furthermore, a superior survival (up to  
27 11 years) but accompanied by a higher wear in the polyethylene part  
28 of HA-coated Mallory-Head cups was reported,<sup>6</sup> along with the excellent  
29 long-term fixation of the ABG-1 femoral stems derived from the  
30 osteointegration and proximal seal around the HA coating.<sup>7</sup> HA  
31 coated titanium based endosteal implants have gained significant  
32 use in dental applications. Titanium plasma sprayed (TPS) HA is  
33 most widely used as coating material for endosseous dental implants.  
34 Although coated implants with both TPS and HA show appreciable  
35 rate of success, coating metallic implants with bioactive HA can

1 accelerate the integration process during initial stages of osseointe-  
2 gration and reduce recovery time.<sup>8</sup>

#### 3 **4.2. HA coatings by plasma spraying technique**

4 Plasma spraying deposition technique is frequently utilised to deposit  
5 the HA on a metal substrate. It involves deposition of HA powder  
6 in a heating compartment where it is subsequently melted. Molten  
7 fragments of HA powder are pushed towards and deposited on metal  
8 substrate. To date, the plasma spraying method has enjoyed domi-  
9 nance in application of HA coatings on metal substrates. Consider-  
10 able amount of HA coated implants that were used in early the 1990s  
11 in the US were produced by a plasma spraying technique. Further-  
12 more, plasma spraying technique is a commercially approved method  
13 by US Food and Drug Administration (FDA) for HA coatings on  
14 metal substrates.

15 The plasma spraying process involves transfer of electrical energy  
16 to a plasma generator. This device is sometimes referred to as a “plas-  
17 matron”, which is an X-ray tube like device that consists of cathode  
18 and anode. Different types of ionising gases are used in a plasma-  
19 tron. A direct current supplied to the cathode causes the ionisation of  
20 gases and a plasma flame is produced. The gas forms unstable plasma  
21 that is transformed into gas again. This process is characterised by  
22 withdrawn thermal and kinetic energy which is subsequently used to  
23 deposit the HA particles on a substrate of any shape.

24 Plasma spraying equipment is somewhat complex due to the fact  
25 that many parameters should be carefully chosen in order to attain  
26 the desirable coating results. Spraying HA at low particle tempera-  
27 ture results in low degradation properties, however it lacks mechan-  
28 ical properties due to poor adhesion to the substrate. On the other  
29 hand, spraying HA at high particle temperatures results in good  
30 mechanical properties but exhibits poor biocompatibility due to for-  
31 mation of calcium oxide (CaO). In addition, one of the disadvantages  
32 of plasma sprayed HA coated implants is their degradation. On their  
33 way from plasmatron to substrate, HA particles are subjected to  
34 high temperature fluctuations that provoke its degradation. Forma-  
35 tion of highly dissoluble tricalcium phosphate (TCP), tetracalcium

1 phosphate (TTCP), and amorphous calcium phosphates (ACP) rep-  
2 presents the consequence of degradation.<sup>9</sup>

3 Low pressure plasma spraying (LPPS), aims to ameliorate an  
4 unacceptable porosity and chemical modification of deposited coat-  
5 ings resulted from stereotyped plasma spraying techniques. Increas-  
6 ing the volume of the chamber allows decreasing the pressure in the  
7 range of 2–13 kPa. This subsequently allows increasing the particle  
8 velocity to promote better adhesion and to hinder adverse effects  
9 of gas–metal interaction. However, the LPPS process has drawbacks  
10 in terms of raising the substrate temperature. Heimann and Vu<sup>10</sup>  
11 outlined the characteristics of HA coatings on Ti-6Al-4V substrates  
12 deposited by a LPPS process. They concluded that subjecting the  
13 HA powder to preliminary sintering at  $\approx 1300^\circ\text{C}$  promotes better  
14 adhesion strength and prolonged in vitro stability of the coated layer.  
15 An increased density of HA particles attained by prior sintering was  
16 believed to be the major contributing factor in the final product’s  
17 properties.

### 18 4.3. HVOF technique

19 HVOF technique exploits mixture of oxygen and fuel (Propylene,  
20 Hydrogen, and Propane) fed into the combustion chamber. The con-  
21 tinuous combustion process propels partially melted HA powder from  
22 the nozzle at approx. 800 m/s and deposits it on the substrate sur-  
23 face. The maximum thickness of HA coating from HVOF deposition  
24 technique can reach 6.35 mm with low porosity. Lima *et al.*<sup>11</sup> con-  
25 ducted a study of an *in vitro* behaviour of HVOF sprayed HA on Ti-  
26 6Al-4V via immersing the coatings in simulated bodily fluids (SBF)  
27 for seven days. It was reported that HA coatings are highly crys-  
28 talline and formation of TCP, TTCP, and CaO were not observed.

29 The potential use of HVOF as an alternative technique to attain  
30 the similar or better quality HA coatings, compared to that achieved  
31 by conventional plasma spray technique is widely considered. By  
32 varying the parameters of HVOF process, such as, oxygen flow rate,  
33 propylene flow rate, air flow rate, spray distance and powder flow  
34 rate, the desired final product properties can be achieved. However,

1 further studies, such as on bioactivity and adhesion strength should  
2 be conducted to fully assess the potential of HVOF process.

3 Fernandez *et al.*<sup>12</sup> have performed heat treatment to monitor its  
4 possible effects on bioactivity and chemical/mechanical properties of  
5 HVOF deposited HA coatings. Comparing the several important fac-  
6 tors of raw powder, sprayed, and heat-treated coating as a function  
7 of bond strength, crystallinity, degradation products, phase analysis,  
8 porosity, and surface morphology yielded the following results. Heat-  
9 treated coatings exhibited superior adhesion strength. In addition,  
10 the bonding strength of heat treated coating remained unaltered  
11 when subjected to SBF. On the other hand, as-sprayed coatings  
12 exhibited significant worsening of adhesive strength. It has to be  
13 mentioned that heat treated coatings showed limited bioactivity com-  
14 pared to that of the as-sprayed one. Lower biomimetic ability may be  
15 a contributing factor for decreased porosity of heat-treated coatings.

#### 16 4.4. HVFSFS

17 Another lately emerged thermal spray technique is the HVFSFS pro-  
18 cess, which typically produces HA films of 75–90  $\mu\text{m}$  in thickness.  
19 In this process the feeding system draws the suspension out of a  
20 reservoir and pushes it continuously with controlled flow rate into  
21 the combustion chamber of a HVOF spraying modified torch. Com-  
22 paring the properties of HA coatings deposited with different ther-  
23 mal spray techniques, such as Atmospheric Plasma Spray (APS),  
24 HVOF, and HVFSFS, the efficiencies of HVOF and APS deposited  
25 coatings were higher ( $42.5 \pm 1.5\%$  and  $52.5 \pm 2.5$  respectively as com-  
26 pared to  $13.0 \pm 1.5$  for HVFSFS), while the HVFSFS coatings exhib-  
27 ited better microstructure. In addition, a higher level of crystalline  
28 HA was observed in the coatings deposited by HVOF, compared to  
29 that of APS and HVFSFS. The suspension type, for example water  
30 based or diethylene glycol (DEG) with dispersed nano-HA that can  
31 be employed during the HVFSFS process, affects the final micro-  
32 structural properties of coatings.<sup>13</sup>



#### 1 **4.5. EPD technique**

2 The method of depositing HA via EPD technique has received great  
3 attention in biomedical applications due to its simplicity, relatively  
4 low equipment cost, uniformity, and ability to control the thickness  
5 of the coatings. EPD can be used to process wide range of materials  
6 including metals, ceramics and polymers. Furthermore, by combining  
7 ceramic materials with polymers or metals, it is possible to manufac-  
8 ture unique composite coatings. EPD process is split in two parts:  
9 electrophoresis and deposition. Applied electrical field to stable col-  
10 loidal suspension promotes movement and subsequent deposition of  
11 electrically charged HA powders on a metallic substrate.

12 In order to acquire the desired homogeneity of HA coatings and  
13 its close integration to a substrate, several deposition parameters like  
14 sintering duration, temperature profile, and applied current density  
15 should be carefully chosen. Ti-6Al-4V is typically used as cathode  
16 with gold or gold plated glass plate as anode for constant voltage  
17 electrophoretic deposition. A deposition of several layers is also rec-  
18 ommended to avoid poor mechanical behaviour of HA coatings.

#### 19 **4.6. Physical and chemical vapour deposition** 20 **techniques**

21 PVD represents yet another technique used for HA deposition. Depo-  
22 sition of materials during PVD process is carried out under vacuum  
23 conditions. The process is broken into several steps: (1) Deposition  
24 material is converted into vapour by high energy ion beams; (2)  
25 Vapourised atoms are transported towards the substrate; (3) Con-  
26 densation process of vapourised HA atoms leads to formation of thin  
27 film on metal substrate.

28 Radiofrequency (RF) magnetron sputtering is frequently used to  
29 deposit thin films with good adhesive properties. RF magnetron sput-  
30 tering uses a RF field that generates plasma between a target and  
31 a substrate holder. The target represents the source from where the  
32 materials are ejected, and the substrate is placed in a vacuum chamber.  
33 Negative charge applied to the source causes plasma discharge. The  
34 plasma region produces gas ions which are bombarded towards the  
35 negatively charged target plate. This in turn produces a momentum

1 transfer and ejected atoms are accelerated towards the substrate.  
2 Upon collision with the substrate HA particles form a thin film.

3 Other deposition techniques compatible with HA deposition for  
4 medical applications include ion beam deposition (IBD), sol-gel,  
5 pulsed laser deposition (PLD) and ion beam mixing (IBM). How-  
6 ever, due to their slow deposition rate, these techniques have been  
7 rarely used for HA coatings on a large scale.

8 CVD differs from PVD, in that it deposits the solid material  
9 rather than vapourised one. CVD is a deposition technique where  
10 precursor gases are decomposed upon interaction with the heated  
11 substrate. During decomposition they form solid phase. CVD has sev-  
12 eral advantages over PVD in that it does not need ultra-high vacuum  
13 for operation. Controlling the stoichiometry can be easily performed  
14 by monitoring flow rates of precursors. Notably, novel flame assisted  
15 chemical vapour deposition (FACVD) technique is believed to have  
16 a huge potential for HA coatings. Principles of FACVD approx-  
17 imate that of CVD, however, avoiding the utilisation of chamber  
18 for promoting the chemical reactions makes this technique relatively  
19 inexpensive.

#### 20 **4.7. CoBlast<sup>TM</sup> process**

21 CoBlast<sup>TM</sup> process represents the novel and promising coating tech-  
22 nology with reported excellent osteoconductivity and osseointegrity  
23 of HA films.<sup>14</sup> This process of coating is chemistry free, non-vacuum  
24 and is performed at ambient temperatures. Dopant materials can be  
25 deposited on the surface of any reactive metal. CoBlast<sup>TM</sup> is a vari-  
26 ation of standard grit blasting. Conventional grit blasting is mainly  
27 used for surface roughening and material removal, while CoBlast<sup>TM</sup>  
28 can be employed for HA material deposition. The significant differ-  
29 ence between this process and other coating deposition techniques  
30 is that dopant is trapped in the metal oxide layer of the surface.  
31 Another distinct advantage of the CoBlast<sup>TM</sup> process is that dur-  
32 ing deposition HA is unaltered. These features eliminate the need  
33 of HA heat treatment prior to its deposition and avoid formation of  
34 the calcium phosphate, which in turn hinders bonding between host  
35 bone and implant. The deposition process is fairly simple and easy  
36 to implement in manufacturing environment.

430 *O. Korostynska et al.*

1 During CoBlast<sup>TM</sup> process, two blast jets are employed simultane-  
2 ously. One jet blasts an abrasive grit that abrades and churns up the  
3 metal surface, baring the metal beneath the oxide layer, while the sec-  
4 ond jet is used to deposit HA coating material on exposed surface. In  
5 addition, compared to widely used plasma spray technique, produc-  
6 tion flow of CoBlast<sup>TM</sup> combines roughening and deposition of HA  
7 in a single step. Therefore, CoBlast<sup>TM</sup> allows pointing the coating on  
8 particular area of substrate and eliminates the masking procedure.  
9 The process integrates the coating material into the reformed oxide  
10 layer of metal surface by tribochemical bonding and interlocking.  
11 Thus, the deposited bioceramic material is not prone to alteration  
12 and delamination.

13 Layer of HA deposited by CoBlast<sup>TM</sup> is  $\leq 10 \mu\text{m}$  in thickness  
14 and elicits better adhesion properties, based on the results of Ameri-  
15 can Society for Testing and Materials (ASTM) tensile (79 MPa) and  
16 shear (48 MPa) stresses. Notably, EnBIO has dispatched OsteoZip<sup>TM</sup>  
17 HA surface that aims to promote rapid integration and fixation of  
18 orthopaedic implants with host bone. It may be used as a coating  
19 material for metal implants in orthopaedic applications. Osteozip<sup>TM</sup>  
20 is HA surface sprayed by novel CoBlast<sup>TM</sup> technique that aims  
21 to enhance osseous integration and speed up the bonding process  
22 between the orthopaedic implant and bone.

## 23 5. Thick Film Technology

24 The manufacture of thick film structures for medical sensing devices  
25 can be achieved using a number of approaches, with screen-printing  
26 being the most popular. This is due to the fact that this technique  
27 is cost-effective, robust, and versatile, giving the opportunity to pro-  
28 duce complex structures with a range of materials, from biocom-  
29 compatible metals and coatings to polymers, printed on virtually any  
30 substrate.

31 Therefore, the screen-printing technique was chosen as a way to  
32 produce thick HA films so that their pressure sensing potential can  
33 be assessed. This in turn leads to the unique opportunity to deposit  
34 functional HA films in a broad range of medical applications.

1 Thick-film technology remains a popular manufacturing method  
2 for many years and its main application is in the production of hybrid  
3 microelectronic circuits for use in telephones, automotive electronics,  
4 and especially for a broad variety of sensors, including gas sensors,  
5 pressure, humidity, radiation, and for biomedical applications.

6 The major steps in the screen-printing of thick-film structures  
7 are printing, drying and firing/curing the functional layer at ele-  
8 vated temperature.<sup>15</sup> Modern screen-printing technological process  
9 normally automatically forces an ink or paste through a stainless  
10 steel mesh, using a squeegee onto the substrate below it. The sub-  
11 strate acts as a physical support for the thick film and the choice  
12 of the substrate material is also dictated by the considerations of  
13 mechanical strength, smoothness of surface texture to promote good  
14 film adhesion, chemical, and physical compatibility with the fired  
15 thick film, high electrical insulation resistance to prevent electrical  
16 leakage currents between closely spaced conductor lines, low thermal  
17 expansion coefficient to prevent thermal mismatch, high thermal sta-  
18 bility to prevent decomposition during processing, biocompatibility  
19 if required, and not least the desire of cost-effectiveness.

20 The quality of the printed layer is largely affected by the choice  
21 of mask. Elements such as the material used, the type of coating, the  
22 accuracy of the pattern, the alignment of the pattern to the mesh,  
23 the frame type and method of mounting and supporting the frame  
24 for printing are important. Polyester mesh was used in this work and  
25 the semi-automatic screen printer model was DEK 1022.

26 The main requirement for the thick film paste is that it must be  
27 able to flow through the screen and retain its intended shape on the  
28 substrate beneath. This depends largely on the pastes flow proper-  
29 ties, viscosity, and particles size in particular.<sup>16</sup> Cermet pastes have  
30 a functional ingredient, solvent, temporary binder and permanent  
31 binder and require firing at high temperatures. For polymer pastes,  
32 there is no temporary binder and pastes are dried at temperatures  
33 in the region of 120°C–250°C.

34 The main purpose of the squeegee is to bring the screen into  
35 contact with the substrate, push the paste through the stencil to  
36 the substrate, to shear the paste level with the top of the screen in

432 *O. Korostynska et al.*

1 order to obtain uniform thickness and to control the rate at which  
2 the screen peels away from the substrate. A classic ‘trailing edge’  
3 squeegee type was used throughout this work to print the HA layers  
4 and Ag electrodes, as it is flexible and exerts uniform pressure on the  
5 screen.

6 After the screen-printing the substrates were left to stand in air  
7 for 5 min to allow the paste to settle. To remove the organic solvents  
8 from the printed layer, so that it can take its final form and be  
9 immune to smudging, the substrates with printed silver electrodes  
10 were then placed in a conventional oven at temperature of 100°C  
11 for 1 h. Drying also improves adhesion of the printed layers to the  
12 substrate.

13 The term “firing” refers to a high temperature cycle of up to  
14 1000°C, the purpose of which is to remove the temporary or organic  
15 binder from the film, sinter the permanent or inorganic binder, and to  
16 develop the electrical properties of the paste, while ensuring the film’s  
17 adequate adherence to the substrate. However, low-temperature sil-  
18 ver paste was used for this work to avoid the firing step. This reduced  
19 the cost of manufacturing without compromising the films quality  
20 and is more in line with the requirements of medical devices industry.

21 The film layers produced using the screen-printing technology typ-  
22 ically measure 5–200  $\mu\text{m}$ , and can be deposited on virtually any  
23 suitably prepared substrate. The main attractions of screen-printing  
24 for medical devices are its versatility, reliability and reproducibil-  
25 ity, and cost-effectiveness even at small or medium scale production.  
26 For highly specialised application, thick film technology offers the  
27 manufacture of devices that are robust, can be miniaturised, can be  
28 integrated onto the same substrate as the electronics and the printed  
29 pattern can act as an active sensing component.<sup>15,17</sup>

## 30 **6. Manufacture and Testing of Pressure Sensing** 31 **Properties of HA Thick Films**

32 To prepare HA paste for screen-printing, 3 g of HA powder with a  
33 typical particle size less than 25  $\mu\text{m}$ , supplied by Cam Bioceram-  
34 ics (the Netherlands) was mixed with 7 wt.% of polyvinyl butanol

1 (PVB) as organic binder and 3 wt.% of glass frit. Further, addition of  
 2 diethylenglycolmonobutylether as a solvent improved the rheological  
 3 properties of paste.

4 Upon deposition of each layer, films were allowed to dry at room  
 5 temperature for 10 min and then cured for 1 h in an oven. These  
 6 steps were successfully repeated before depositing additional layers  
 7 on each sample to produce films with various thicknesses.

8 Characterisation of electrical properties based on real-time  
 9 changes in the capacitance values as a function of applied pressure  
 10 was performed at 10 kHz using the HP Impedance Analyser  
 11 4192A LF. Area of HA layer subjected to pressure application was  
 12  $3.17 \cdot 10^{-5} \text{ m}^2$ . Pressure ranging from 15 to 140 MPa was applied on  
 13 samples covered with 14  $\mu\text{m}$ , 20  $\mu\text{m}$ , and 32  $\mu\text{m}$  thick HA films. Dur-  
 14 ing the experiments the pressure applied on the samples was grad-  
 15 ually increased and the changes in the values of capacitance were  
 16 recorded with the sampling rate of 1 s.

17 **7. Experimental Results Overview: Reversible**  
 18 **Pressure-induced Changes in HA**

19 Figure 1 depicts a plot of real time changes of capacitance values  
 20 as a function of gradually applied pressure to 14  $\mu\text{m}$  thick HA film.  
 21 Screen printed sample exhibits the direct relationship between the

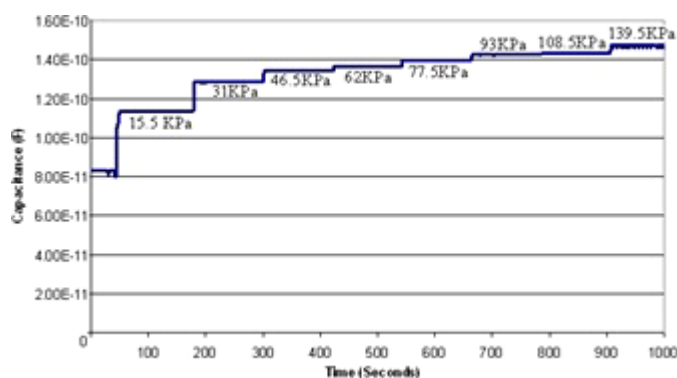


Fig. 1. Real-time capacitance changes due to pressure application in 14  $\mu\text{m}$  thick HA film.

434 O. Korostynska et al.

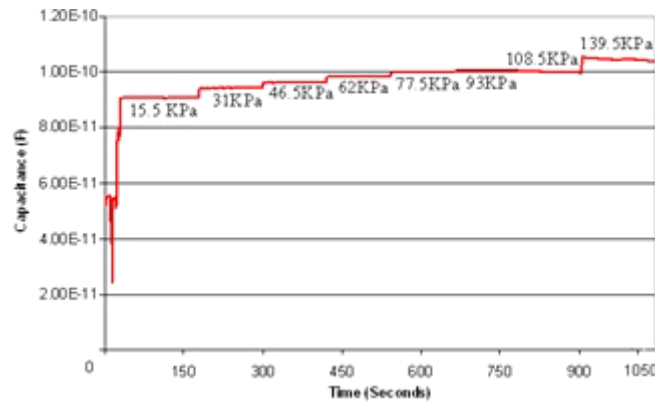


Fig. 2. Real-time capacitance changes due to pressure application in 20  $\mu\text{m}$  thick HA film.

1 increase in pressure and the value of capacitance. The plot can be  
 2 clearly partitioned in two parts. Application of 15.5 kPa yields rapid  
 3 change in the value of capacitance and this phenomenon remains  
 4 the same for further loading. However it can be discerned that rapid  
 5 changes in capacitance values of 14  $\mu\text{m}$  thick HA sample seems to  
 6 dissipate. Minor changes in capacitance can be observed as the pres-  
 7 sure overlaps the 46.5 kPa value and reaches the value of 147 pF  
 8 as it is subjected to 139.5 kPa.

9 Real-time capacitance changes as a function of applied pressure  
 10 to 20  $\mu\text{m}$  thick HA layer are depicted in Figure 2. A sudden shift in  
 11 capacitance value from 55.2 to 90.5 pF in the first stage of pressure  
 12 application is clearly noticeable. Further increases in the capacitance  
 13 values are minor, similarly to 14  $\mu\text{m}$  film behaviour. In addition,  
 14 capacitance value seems to stabilise in the pressure range from 93  
 15 to 108.5 kPa, while an upward shift is noticeable once the pressure  
 16 equalises the value of 139.5 kPa. At the final stage of measurement  
 17 capacitance reaches the value of 10 nF.

18 In line with thinner films, 32  $\mu\text{m}$  thick HA layers showed an appre-  
 19 ciable increase in capacitance from 46.6 to 63.8 pF when subjected  
 20 to 15.5 kPa, with graduate but less pronounced further increase in  
 21 capacitance with load, reaching 70.5 pF at 139.5 kPa. Notably, these  
 22 results correlate with the theory as set in Section 2, specifically the

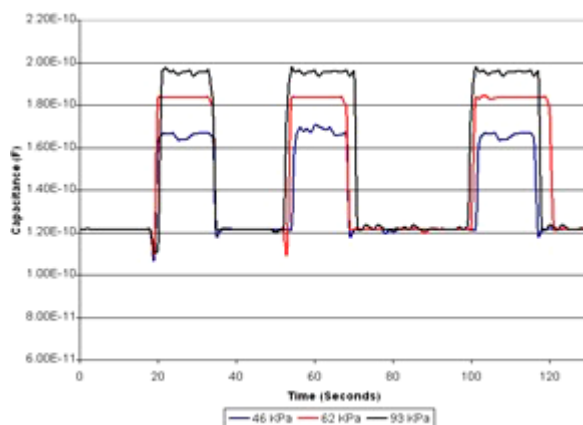


Fig. 3. Application and removal of various amount of pressure on  $14 \mu\text{m}$  HA sample.

1 applied pressure results in increased capacitance values, which is  
 2 inferred to be due to the film thickness reduction/film compression.

3 In order to further investigate the possible piezoelectric effect in  
 4 screen printed HA thick films, they were subjected to a series of load-  
 5 ing and subsequent unloading. In particular, HA films were subjected  
 6 to 46, 62, and 93 kPa pressure. Upon changing the capacitance val-  
 7 ues, the load was kept for several seconds for reliable measurements.  
 8 Once the changes were observed, applied load was released to monitor  
 9 the reversal of capacitance values. Steps of loading and unload-  
 10 ing were repeated for three consecutive times to address response-  
 11 repeatability issues. Figure 3 illustrates the behaviour of  $14 \mu\text{m}$  thick  
 12 sample subjected to various amount of pressures during the load-  
 13 ing/unloading tests.

14 Analysing this data reveals that the application of pressure yields  
 15 sudden shift in the capacitance, while upon removal of it, the capac-  
 16 itance falls to its value in unloaded state. Furthermore, behaviour  
 17 of the sample upon loading with the same amount of pressure and  
 18 subsequent withdrawal of it closely approximates that exhibited in  
 19 the previous load/unload step. This type of behaviour is replicated  
 20 for various amounts of pressure. Loading/unloading while utilising  
 21 the same values of pressure was also performed on  $20 \mu\text{m}$  and  $32 \mu\text{m}$   
 22 samples with identical trend.



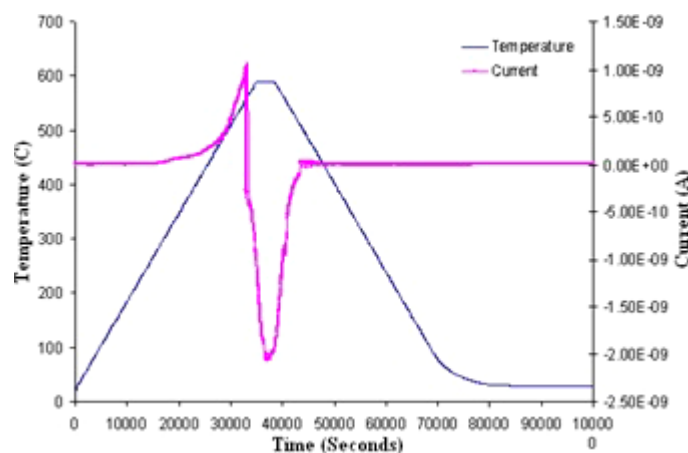
436 O. Korostynska *et al.*

Fig. 4. Pyroelectric surface charge in screen-printed HA thick films (Reprinted with permission from Ref. 18.)

1 Another objective of pressure application experiments was to  
 2 identify the possible pyroelectric effect in screen printed HA samples.  
 3 Capacitance values of all the samples tested in aforementioned exper-  
 4 iments underwent noticeable changes upon application of pressure.  
 5 In addition, removal of pressure was instantly followed by returning  
 6 the capacitance values to their initial values.

7 To further confirm the pyroelectric effect in screen-printed HA  
 8 thick films, they were subjected to poling at  $4 \text{ kV/cm}^2$  for 1 h.<sup>18</sup>  
 9 Subjecting the sample to the peak temperature of  $550^\circ\text{C}$  while the  
 10 heating/cooling rate of  $3^\circ\text{C/min}$  showed a pyroelectric behaviour of  
 11 HA thick films. Figure 4 reproduces the pyroelectric effect that took  
 12 place during poling the sample in an aforementioned environment  
 13 and shows the charge storing capabilities of HA films.<sup>18</sup>

14 Pressure induced changes of capacitance further confirms piezo-  
 15 electric and pyroelectric nature of HA postulated by Tofail *et al.*,<sup>19</sup>  
 16 who measured pyroelectric constant of poled HA ceramics to be in  
 17  $0.1 - 40 \text{ nC cm}^{-2} \text{ K}^{-1}$  range at  $300 - 500^\circ\text{C}$ . Piezo and pyroelectric  
 18 al properties of un-poled HA thin films was noted in the study by  
 19 Lang *et al.*,<sup>20</sup> during which HA thin films were spin-coated on silicon  
 20 wafers.

1 These properties of screen printed HA thick films make them  
2 attractive option for real-time *in vivo* pressure sensors, as response  
3 and recovery times were ranging from 0.9 to 3.2 s for HA films, with  
4 shorter time for thinner films. However, thicker sample showed higher  
5 sensitivity to pressure as compared to relatively thin ones, not least  
6 due to a porous nature of thick HA films.

## 7 8. Conclusions

8 Thick film technology, namely screen printing technique, was utilised  
9 to deposit various thickness of novel HA thick film on alumina sub-  
10 strates, with the aim of their possible implementation in the field  
11 of biomedical industry. Specifically, HA films can be used as a coat-  
12 ing for bone and dental implants, as well as biocompatible pressure  
13 sensors, due to their reversible changes in electrical properties under  
14 the influence of applied pressure. The additional advantage of the  
15 coating in the form of screen-printed thick films is that due to the  
16 technology's versatility, it can be produced on flexible substrate in  
17 any shape and size to suit the needs of various patients.

## 18 References

- 19 1. A. Sparnell, Aniket and A. El-Ghannam, "Machining of a bioactive nanocom-  
20 posite orthopedic fixation device", *J. Biomed. Mater. Res. — Part B Appl.*  
21 *Biomater.* **100 B**, 1545–1555 (2012).
- 22 2. J.-P. Vidalain, "Long term results with a fully HA-coated prosthesis —  
23 results, lessons, and comments from the series performed by the ARTRO  
24 group (15-year experience)", *Key Eng. Mater.* **192–195**, 1021–1024 (2001).
- 25 3. M. Tarala, D. Waanders, J.E. Biemond, G. Hannink, D. Janssen, P. Buma,  
26 N. Verdonchot "The effect of bone ingrowth depth on the tensile and shear  
27 strength of the implant-bone e-beam produced interface", *J. Mater. Sci.*  
28 *Mater. Med.* **22**, 2339–2346 (2011).
- 29 4. M.J. Coathup, J. Blackburn, A.E. Goodship, J.L. Cunningham, T. Smith,  
30 G.W. Blunn "Role of hydroxyapatite coating in resisting wear particle migra-  
31 tion and osteolysis around acetabular components," *Biomaterials* **26**, 4161–  
32 1469 (2005).
- 33 5. J.A. Epinette, M.T. Manley, "Uncemented stems in hip replacement —  
34 hydroxyapatite or plain porous: Does it matter? Based on a prospective study  
35 of HA Omnifit stems at 15-years minimum follow-up," *Hip. Int.* **18**, 69–74  
36 (2008).

438 O. Korostynska et al.

- 1 6. M. Gottlieb, O. Rahbek, P.F. Ottosen, K. Soballe, M. Stilling, "Superior 11-year survival but higher polyethylene wear of hydroxyapatite-coated  
2 Mallory-Head cups," *Hip. Int.* **22**, 35–40 (2012).
- 3 7. R. Bidar, P. Kouyoumdjian, E. Munini, G. Asencio, "Long-term results of  
4 the ABG-1 hydroxyapatite coated total hip arthroplasty: analysis of 111 cases  
5 with a minimum follow-up of 10 years," *Orthop Traumatol. Surg. Res.* **95**,  
6 579–587 (2009).
- 7 8. Z. Strnad, J. Strnad, C. Povysil, K. Urban, "Effect of plasma-sprayed hydrox-  
8 yapatite coating on the osteoconductivity of commercially pure titanium  
9 implants," *Int. J. Oral. Maxillofac. Implants.* **15**, 483–490 (2000).
- 10 9. R.Z. LeGeros, J.P. LeGeros, "In situ characterization of degradation behavior  
11 of plasma-sprayed coatings on orthopedic and dental implants," *Adv. Sci.*  
12 *Technol.* **49**, 203–211 (2006).
- 13 10. R.B. Heimann, T.A. Vu, "Low-pressure plasma-sprayed (LPPS) bioce-  
14 ramic coatings with improved adhesion strength and resorption resistance,"  
15 *J. Thermal Spray Technol.* **6**, 145–149 (1997).
- 16 11. R.S. Lima, K.A. Khor, H. Li, P. Cheang, B.R. Marple, "HVOF spraying  
17 of nanostructured hydroxyapatite for biomedical applications," *Mater. Sci.*  
18 *Eng.: A* **396**, 181–187 (2005).
- 19 12. J. Fernández, M. Gaona, J.M. Guilemany, "Effect of heat treatments on  
20 HVOF hydroxyapatite coatings," *J. Thermal Spray Technol.* **16**, 220–228  
21 (2007).
- 22 13. R. Gadow, A. Killinger, N. Stiegler, "Hydroxyapatite coatings for biomedical  
23 applications deposited by different thermal spray techniques," *Surface and*  
24 *Coatings Technology* **205**, 1157–1164 (2010).
- 25 14. P. O'Hare, B.J. Meenan, G.A. Burke, G. Byrne, D. Dowling, J.A. Hunt,  
26 "Biological responses to hydroxyapatite surfaces deposited via a coincident  
27 microblasting technique," *Biomaterials* **31**, 515–522 (2010).
- 28 15. D. Morris, K. Arshak, A.A., O.K., "Metal Oxide Nanostructures for  
29 Advanced Pressure Sensing Applications," in *Metal Oxide Nanostructures*  
30 *and Their Applications* (American Scientific Publishers, 2010).
- 31 16. K. Arshak, O. Korostynska, *Advanced Materials and Techniques for Radia-  
32 tion Dosimetry* (Artech House, 2006).
- 33 17. M. Salazar-Alvarez, O. Korostynska, A. Mason, A. Al-Shamma'a, J.C.  
34 Cooney, E. Magner, S.A.M. Tofail, "Label free detection of specific protein  
35 binding using a microwave sensor," *Analyst* **139**, 5335–5338 (2014).
- 36 18. O. Korostynska, G. Gigilashvili, A.A. Gandhi, S.A.M. Tofail, "High temper-  
37 ature induced pyroelectricity in screen-printed Hydroxyapatite thick films,"  
38 in IEEE 14<sup>th</sup> International Symposium on Electrets, ISE 2011, Montpellier,  
39 France, August 28–31, (2011).
- 40 19. S.A.M. Tofail, C. Baldisserri, D. Haverty, J.B. McMonagle, J. Erhart, "Pyro-  
41 electric surface charge in hydroxyapatite ceramics," *J. Appl. Phys.* **106** (2009).
- 42 20. S.B. Lang, S.A.M. Tofail, A.A. Gandhi, M. Gregor, C. Wolf-Brandstetter,  
43 J. Kost, S. Bauer, M. Krause, "Pyroelectric, piezoelectric, and photoeffects  
44 in hydroxyapatite thin films on silicon," *Appl. Phys. Lett.* **98** (2011).
- 45

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